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For: OXYNITRIDE PHOSPHOR AND PRODUCTION PROCESS THEREOF, AND LIGHT-EMITTING DEVICE USING OXYNITRIDE PHOSPHOR		

**VERIFICATION OF ENGLISH TRANSLATION**

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Sir:

I, Keiichi GONJOU, declare that I am conversant in both the Japanese and English languages and that the English translation as attached hereto is an accurate translation of Japanese Patent Application No. 2003-028610 filed February 5, 2003.

Signed this 23rd day of May, 2008



Keiichi GONJOU

PATENT OFFICE  
JAPANESE GOVERNMENT

This is to certify that the annexed is a true copy of the following application as filed with this Office.

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Item: Specification	1 copy
Item: Drawings	1 copy
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Proof Yes

[DOCUMENT] Specification

[TITLE OF THE INVENTION]

LIGHT-EMITTING DEVICE USING OXYNITRIDE PHOSPHOR

[CLAIMS]

[CLAIM 1]

An oxynitride phosphor comprising: at least one or more of Group II elements selected from the group consisting of Be, Mg, Ca, Sr, Ba and Zn; at least one or more of Group IV elements selected from the group consisting of C, Si, Ge, Sn, Ti, Zr and Hf; and a rare earth element being as an activator R.

[CLAIM 2]

The oxynitride phosphor according to claim 1, comprising O and N and a weight ratio of O and N is set so that N is within a range of 0.2 to 2.1 per 1 of O.

[CLAIM 3]

An oxynitride phosphor represented by a general formula of  $L_xM_yO_zN_{((2/3)X+(4/3)Y-(2/3)Z)} \cdot R$  (L is at least one or more of Group II elements selected from the group consisting of Be, Mg, Ca, Sr, Ba and Zn. M is at least one or more of Group IV elements selected from the group consisting of C, Si, Ge, Sn, Ti, Zr and Hf. O is an oxygen element. N is a nitrogen element. R is a rare earth element.  $0.5 < X < 1.5$ ,  $1.5 < Y < 2.5$ , and  $1.5 < Z < 2.5$ ).

[CLAIM 4]

An oxynitride phosphor represented by a general formula of  $L_xM_yQ_tO_zN_{((2/3)X+(4/3)Y+T-(2/3)Z)} \cdot R$  (L is at least one or more of Group II elements selected from the group consisting of Be, Mg, Ca, Sr, Ba and Zn. M is at least one or more of Group IV elements selected from the group consisting of C, Si, Ge, Sn, Ti, Zr and Hf. Q is at least one or more of Group III elements selected from the group consisting of B, Al, Ga and In. O is an oxygen element. N is a nitrogen element. R is a rare earth element.  $0.5 < X < 1.5$ ,  $1.5 < Y < 2.5$ ,  $0 < T < 0.5$ , and  $1.5 < Z < 2.5$ ).

[CLAIM 5]

The oxynitride phosphor according to claims 3 or 4, wherein said X, said Y and said Z are  $X = 1$ ,  $Y = 2$ , and  $Z = 2$ .

[CLAIM 6]

The oxynitride phosphor as in one of claims 1, 3 and 4, wherein 70 weight % or more of said R is Eu.

[CLAIM 8]

The oxynitride phosphor as in one of claims 1 to 7; which has a luminescence spectra having a peak wavelength in a range of from blue green to yellow red region.

[CLAIM 9]

The oxynitride phosphor as in one of claims 5 to 8; of which at least a portion is crystal.

[CLAIM 10]

The oxynitride phosphor according to claim 9, wherein said crystal has a unit lattice of the orthorhombic system.

[CLAIM 11]

The oxynitride phosphor as in one of claims 1 to 10, wherein an excitation spectrum which has a luminescence intensity excited by light of 370nm higher than luminescence intensity excited by light of 500nm.

[CLAIM 12]

The oxynitride phosphor as in one of claims 1 to 11, comprising 2 or more of Group II elements selected from the group consisting of Be, Mg, Ca, Sr, Ba and Zn.

[CLAIM 13]

The oxynitride phosphor as in one of claims 1 to 12, comprising Sr and Ca in a molar ratio of  $Sr : Ca = 6 : 4$  to  $9 : 1$ .

[CLAIM 14]

The oxynitride phosphor as in one of claims 1 to 12, comprising Sr and Ba in a molar ratio of  $Sr : Ba = 6 : 4$  to  $9 : 1$ .

[CLAIM 15]

The oxynitride phosphor as in one of claims 1 to 12, comprising Ca and Ba in a molar ratio of Ca : Ba = 6 : 4 to 9 : 1.

[CLAIM 16]

A process for production of an oxynitride phosphor comprising;

a first step of mixing raw materials containing the nitride of L (L is at least one or more of Group II elements selected from the group consisting of Be, Mg, Ca, Sr, Ba and Zn, the nitride of M (M is at least one or more of Group IV elements selected from the group consisting of C, Si, Ge, Sn, Ti, Zr and Hf), the oxide of M, and the oxide of R (R are one or more rare earth elements), and

a second step of firing the mixture obtained in said first step.

[CLAIM 17]

The process for production of an oxynitride phosphor according to claim 16;

wherein a nitride of R is used in place of said oxide of R, or together with said oxide of R.

[CLAIM 18]

The process for production of an oxynitride phosphor as in one of claims 16 to 17;

wherein a compound of Q (Q is at least one or more of Group III elements selected from the group consisting of B, Al, Ga and In) is further mixed in said first step.

[CLAIM 19]

The process for production of an oxynitride phosphor as in one of claims 16 to 19;

wherein said nitride of L, said nitride of M and said oxide of M are adjusted in molar ratios of  $0.5 < \text{the nitride of L} < 1.5$ ,  $0.25 < \text{the nitride of M} < 1.75$  and  $2.25 < \text{the oxide of M} < 3.75$ .

[CLAIM 20]

The process for production of an oxynitride phosphor according to claims 16 or 19;

wherein at least a portion of the raw material of said nitride of L is substituted with at least either of the oxide of R and a nitride of R.

[CLAIM 21]

The oxynitride phosphor produced by the process as in one of claims 16 to 20.

[DETAILED DESCRIPTION OF THE INVENTION]

[0001]

The present invention relates to a phosphor which emit a light by being excited by light, electromagnetic waves such as X-rays, electron beam, and specifically, relates to a light-emitting device for usual illuminations such as a fluorescent lamp, illuminations mounted on a car, back lights for liquid crystal, displays and the like. Specifically, the present invention relates to a white color and multi-color light-emitting device using a semiconductor light-emitting element.

[TECHNICAL FIELD TO WHICH THE INVENTION PERTAINS]

[0002]

[PRIOR ART]

A light-emitting device using light-emitting elements is a small size and superior in electric power efficiency, and emits fresh color. Further, said light-emitting elements have characteristics that there is no fear of a burnt-out light bulb because of a semiconductor element and they are superior in initial drive property and resistant in vibration and the repetition of on-off lighting. Since the light-emitting elements have such superior characteristics, a light-emitting device using semiconductor light-emitting elements such as an LED and a LD has been utilized as various light sources.

[0003]

There is developed a light-emitting device which emits a luminescence color different from the light of the light-emitting elements by partially or wholly converting the wavelength of the light of the light-emitting elements and mixing said wavelength-converted light with the light of light-emitting elements not subjected to wavelength conversion to release light.

[0004]

Among these light-emitting devices, a white color light-emitting device has been required in wide fields such as usual illuminations such as a phosphorescent lamp,

illuminations mounted on a car, displays and back lights for liquid crystal.

[0005]

The luminescence color of a light-emitting device using a white color semiconductor light-emitting element is obtained by the theory of color mixture. Blue light released from a light-emitting element is irradiated in a phosphor layer, then repeats absorption and scattering several times in the layer, and then, is released to outside. On the other hand, the blue light absorbed in the phosphor works as an excitation light source and emits yellow fluorescent light. The mixture of the yellow light and the blue light is visualized as white to human eyes.

[0006]

For example, a blue color light-emitting element is used as the light-emitting element, and a phosphor is thinly coated on the surface of said blue color light-emitting element. Said light-emitting element is a blue color light-emitting device using an InGaN-base material. Further, the phosphor uses a YAG-base phosphor represented by the composition formula of  $(Y,Gd)_3(Al,Ga)_5O_{12}:Ce$ .

[0007]

Further, there has been recently reported a white color light-emitting device combining a phosphor which emits blue light and a YAG-base phosphor which emits yellow light using light-emitting elements of visible light at a short wavelength side region. In this case, the YAG-base phosphor which emits yellow light is hardly excited by light of visible light at the short wavelength side region and does not emit light. Accordingly, a blue color-base phosphor is excited by said light-emitting element to emit blue light. Then, the YAG-base phosphor is excited by said blue light to emit yellow light. Thus, white color light is emitted by the color mixture of the blue light of the blue color-base phosphor with the yellow light of the YAG-base phosphor. There is an advantage that the color of the light emitting device is not affected by the changing of the luminescent spectra owing to dispersion of production since the human eyes can not sense a light in that range.

[0008]



Various phosphors are developed as the phosphor used in said light-emitting device.

[0009]

For example, an oxide-base phosphor using a rare earth metal element for a luminescence center has been widely known, and a portion of the phosphor is already practically used. However, a nitride phosphor and an oxynitride phosphor are seldom studied, and a study report is scarcely reported. For example, there is an oxynitride glass phosphor which is represented by Si-O-N, Mg-Si-O-N, Ca-Al-Si-O-N and the like (JP-A-2001-214162 : hereinafter, referred to as the patent literature 1). Further, there is an oxynitride glass phosphor represented by Ca-Al-Si-O-N in which Eu was activated (JP-A-2002-76434 : hereinafter, referred to as the patent literature 2).

[0010]

[Patent Document 1]      JP-A-2001-214162

[Patent Document 2]      JP-A-2002-76434

[0011]

#### [PROBLEM TO BE SOLVED BY THE INVENTION]

However, in a light-emitting device using light-emitting elements at a near ultraviolet region as an excitation light source, there is used double step excitation that a blue light-base phosphor is excited by said light-emitting elements and the YAG-base phosphor is excited by said excited light, therefore while light having high efficiency is hardly obtained. Accordingly, there is desired a phosphor emitting green light to yellow light whose wavelength was directly converted by light of visible light at a short wavelength side region.

[0012]

Further, a white color light-emitting device combining a phosphor and a light-emitting element of visible light at a short wavelength side region is not produced yet and the light-emitting device practically used is not commercially available. Accordingly, a phosphor which efficiently emits light at a short wavelength side region of visible light is

desired.

[0013]

Further, the above-mentioned oxynitride phosphors have low luminescence brightness and are insufficient for being used for the light-emitting device. Further, since the oxynitride glass phosphor is a glass body, it is hardly processed in general.

[0014]

Accordingly, an object of the present invention is to provide a phosphor which is excited by an excitation light source at an ultraviolet to visible light region and which has a blue green to yellow luminescence color that is wavelength converted.

[0015]

#### [MEANS FOR SOLVING PROBLEM]

To solve aforementioned problem, the present invention relate to a oxynitride phosphors containing at least one or more of Group II elements selected from the group consisting of Be, Mg, Ca, Sr, Ba and Zn, at least one or more of Group IV elements selected from the group consisting of C, Si, Ge, Sn, Ti, Zr and Hf, and a rare earth element being an activator, R. With this, the oxynitride phosphor which has a high brightness can be obtained.

[0016]

It is preferable that the oxynitride phosphor contains O and N in the composition and the weight ratio of said O and said N so that N is within a range of 0.2 to 2.1 per 1 of O. The oxynitride phosphor which can be efficiently excited by light from an excitation light source and has a luminescence color at a blue green to yellow region and high luminous efficiency is provided.

[0017]

The present invention relate to an oxynitride phosphor which is represented by the general formula,  $L_xM_yO_zN_{((2/3)X+(4/3)Y-(2/3)Z)}:R$  or  $L_xM_yQ_TO_zN_{((2/3)X+(4/3)Y+T-(2/3)Z)}:R$  (L is at least one or more of Group II elements selected from the group consisting of Be, Mg, Ca, Sr, Ba and Zn. M is at least one or more of Group IV elements selected from the group

consisting of C, Si, Ge, Sn, Ti, Zr and Hf. Q is at least one or more of Group III elements selected from the group consisting of B, Al, Ga and In. O is an oxygen element. N is a nitrogen element. R is a rare earth element.  $0.5 < X < 1.5$ ,  $1.5 < Y < 2.5$ ,  $0 < T < 0.5$ , and  $1.5 < Z < 2.5$ ). The oxynitride phosphor is excited by light in a range from near ultraviolet to a short wavelength side region of visible light and has a luminescence peak at a blue green to yellow region. The oxynitride phosphor has a stability same as or more than YAG phosphor. In addition, since the oxynitride phosphor is not glass (amorphous) but powder or particles having a crystal as a emission portion, it can be made easily. Said X, Y, T, Z set in fore-mentioned range make it possible to provide a phosphor having a high emission efficiency. That is, a crystal layer with efficient emission is formed in said range. The emission efficiency is lowered out of said range. In said range, a crystal layer capable of emitting efficiently is formed. Contrast with this, the emission efficiency is lowered out of the range.

[0018]

The composition may be represented by  $L_xM_yO_zN_{((2/3)X+(4/3)Y-(2/3)Z-\alpha)}R$  or  $L_xM_yQ_tO_zN_{((2/3)X+(4/3)Y+T-(2/3)Z-\alpha)}R$  ( $R \leq \alpha < 1$ ). The reason is that the oxynitride phosphor results also occasionally in a loss of nitrogen. Further, the nearer to zero the  $\alpha$  is, the better the crystallinity of a crystal phase is, therefore the luminescence brightness is enhanced.

[0019]

The fore-mentioned X, the fore-mentioned Y and the fore-mentioned Z are preferably  $X = 1$ ,  $Y = 2$ , and  $Z = 2$ . At said composition, their crystallinity can be bettered, and the luminescence efficiency can be enhanced.

[0020]

Eu is preferably 70% by weight or more among R in order to obtain high luminescence efficiency. The rare earth metal element represented by the fore-mentioned R is preferably Eu in order to obtain high luminescence efficiency. Using Eu in said range make it possible to obtain a high efficiency.

[0021]

The oxynitride phosphors related to the present invention are excited by light from an excitation light source having a luminescence peak wavelength at 490nm or less, and have luminescence spectra having luminescence peak wavelengths at a longer wavelength side than the fore-mentioned luminescence peak wavelength. Namely, the oxynitride phosphors having luminescence with good efficiency is obtained by being excited by light from an excitation light source capable of emitting a light in said range. The excitation light source for exciting the oxynitride phosphors related to the present invention has preferably a luminescence peak wavelength at 240 to 470nm, and more preferably a luminescence peak wavelength at 350 to 410nm.

[0022]

The oxynitride phosphors emits a light in a range from blue green to yellow red region. Namely, even if the YAG-base phosphor having the luminescence peak wavelength at a yellow system is emitted using the ultraviolet or near ultraviolet excitation light, it hardly emits light, but the oxynitride phosphors related to the present invention emit light by the excitation light in said range, and exhibit the high luminescence efficiency. When a blue light is used as a excitation light, the high luminescence efficiency. is obtained.

[0023]

The blue green to yellow red region is represented according to JIS Z8110. Specifically, the blue green to yellow red region means a range of 485 to 610nm.

[0024]

The oxynitride phosphor has a crystal at least partially. The crystal is preferably contained by 50% by weight or more, and more preferably by 80% by weight or more. Namely, the crystalline phases are a principal luminescent portion, and when the portion of the crystalline phases being the luminescent portion is 50% by weight or more, luminescence with good efficiency is obtained. Thus, the more the crystalline phases are, the higher the luminescence brightness can be enhanced. Further, when the portion of

the crystalline phases is much, its production and processing come to be easy.

[0025]

The fore-mentioned crystals have the unit lattice of the rhombic system. According to a structural analysis by the X-ray diffraction pattern of the fore-mentioned phosphors, the unit lattice of the crystal belongs to the rhombic system.

[0026]

The oxynitride phosphors preferably have the excitation spectra in which luminescence intensity by light of 370nm is higher than luminescence intensity by light of 500nm. When they are set thus, the phosphors excited by light at an ultraviolet region exhibit higher brightness than the phosphors excited by light at a blue region. The use of light-emitting elements at an ultraviolet region can constitute a light-emitting device which can exhibit higher luminescence efficiency than the use of light-emitting elements at a blue region.

[0027]

The oxynitride phosphors have preferably 2 or more of Group II elements selected from the group consisting of Be, Mg, Ca, Sr, Ba and Zn, and luminescence properties such as the color tone, luminescence brightness and quantum efficiency can be varied thereby to realize desired luminescence properties.

[0028]

When the oxynitride phosphors contain Sr and Ca, a molar ratio of Sr to Ca is preferably  $\text{Sr} : \text{Ca} = 6 : 4$  to  $9 : 1$ . Further, when the oxynitride phosphors contain Sr and Ba, a molar ratio of Sr to Ba is preferably  $\text{Sr} : \text{Ba} = 6 : 4$  to  $9 : 1$ . Further, when the fore-mentioned first and second oxynitride phosphors contain Ca and Ba, a molar ratio of Ca to Ba is preferably  $\text{Ca} : \text{Ba} = 6 : 4$  to  $9 : 1$ . The oxynitride phosphors having various color tones can be produced by selecting the combination and further selecting the composition ratio within the above-mentioned range. Further, the luminescence efficiency can be improved by selecting it within said range.

[0029]

The production process of the oxynitride phosphors related to a process which has the first step that materials containing the nitride of L (L is at least one or more of Group II elements selected from the group consisting of Be, Mg, Ca, Sr, Ba and Zn, the nitride of M (M is at least one or more of Group IV elements selected from the group consisting of C, Si, Ge, Sn, Ti, Zr and Hf), the oxide of M, and the oxide of R (R is a rare earth element) are mixed, and the second step that the mixture obtained from the first step is calcinated. The phosphors easily produced and processed can be provided by the production process of the oxynitride phosphors related to the present invention. Further, the phosphors with extremely good stability can be provided. Hereat, Li, Na, K, Rb, Cs, Mn, Re, Cu, Ag, Au and the like may be contained in the mother body of the oxynitride phosphors prepared by the production steps of the present production process or the present production process. Provided that, the above-mentioned Li, Na, K and the like are preferably 1000ppm or less based on the weight of the oxynitride phosphors. More preferably, it is preferably 100ppm or less. Because the high luminescence efficiency can be kept so far as it is within said range.

[0030]

The nitride of R is preferably used in place of the fore-mentioned oxide of R, or together with the fore-mentioned oxide of R. The oxynitride phosphors with the high luminescence brightness can be provided thereby.

[0031]

In the fore-mentioned first step, Q (Q is at least one of more of Group III elements selected from the group consisting of B, Al, Ga and In) is further preferably mixed. The particle diameter is enlarged thereby, and the improvement of the luminescence brightness can be designed.

[0032]

The production process of the oxynitride phosphors related to a process in which the fore-mentioned nitride of L, the fore-mentioned nitride of M and the fore-mentioned oxide of M are preferably adjusted at molar ratios of  $0.5 < \text{the nitride of L} < 1.5$ ,  $0.25 < \text{the}$

nitride of M < 1.75 and  $2.25 < \text{the oxide of M} < 3.75$ . The oxynitride phosphors with the composition of  $L_xM_yO_zN_{((2/3)X+(4/3)Y-(2/3)Z)} \cdot R$  or  $L_xM_yQ_tO_zN_{((2/3)X+(4/3)Y+T-(2/3)Z)} \cdot R$  can be provided thereby.

[0033]

At least the portion of the raw material comprising the fore-mentioned nitride of L is preferably substituted with at least either of the oxide of R and the nitride of R. The oxynitride phosphors with the high luminescence efficiency can be provided thereby.

[0034]

The third oxynitride phosphor related to the present invention is an oxynitride phosphor produced by the production process of the fore-mentioned oxynitride phosphors.

[0035]

As described above, the oxynitride phosphors related to the present invention have technical meanings that the phosphors which are excited by light in a range from near ultraviolet to a short wavelength side region of visible light and emit light at a blue green to yellow region can be provided and the light-emitting device with extremely good luminescence efficiency can be provided by being combined with an appropriate excitation light source. A new production process of the oxynitride phosphors can be provided. The oxynitride phosphors related to the present invention can be applied to light emitting device.

[0036]

#### [MODE FOR CARRING OUT THE INVENTION]

The oxynitride phosphor related to the present invention and the production process are illustrated below using the modes of operation and Examples. Provided that the present invention is not limited to embodiments and examples.

[0037]

{ Oxynitride phosphor }

The oxynitride phosphor of the present invention is represented by the general formula of  $L_xM_yO_zN_{((2/3)X+(4/3)Y-(2/3)Z)} \cdot R$ , or  $L_xM_yQ_tO_zN_{((2/3)X+(4/3)Y+T-(2/3)Z)} \cdot R$  {Wherein L is at

least one or more of Group II elements selected from the group consisting of Be, Mg, Ca, Sr, Ba and Zn. M is at least one or more of Group IV elements selected from the group consisting of C, Si, Ge, Sn, Ti, Zr and Hf. Q is at least one or more of Group III elements selected from the group consisting of B, Al, Ga and In. O is an oxygen element. N is a nitrogen element. R is a rare earth element.  $0.5 < X < 1.5$ ,  $1.5 < Y < 2.5$ ,  $0 < T < 0.5$ , and  $1.5 < Z < 2.5$ . The X, Y and Z set in said range make it possible to show a high brightness. Further, in the above-mentioned general formula, X, Y and Z are preferably  $X = 1$ ,  $Y = 2$ , and  $Z = 2$  to show high brightness. The present invention is not limited to the above-mentioned range. Specifically, the oxynitride phosphor represented by  $\text{CaSi}_2\text{O}_2\text{N}_2\cdot\text{Eu}$ ,  $\text{SrSi}_2\text{O}_2\text{N}_2\cdot\text{Eu}$ ,  $\text{BaSi}_2\text{O}_2\text{N}_2\cdot\text{Eu}$ ,  $\text{ZnSi}_2\text{O}_2\text{N}_2\cdot\text{Eu}$ ,  $\text{CaGe}_2\text{O}_2\text{N}_2\cdot\text{Eu}$ ,  $\text{SrGe}_2\text{O}_2\text{N}_2\cdot\text{Eu}$ ,  $\text{BaGe}_2\text{O}_2\text{N}_2\cdot\text{Eu}$ ,  $\text{ZnGe}_2\text{O}_2\text{N}_2\cdot\text{Eu}$ ,  $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{Si}_2\text{O}_2\text{N}_2\cdot\text{Eu}$ ,  $\text{Ca}_{0.5}\text{Ba}_{0.5}\text{Si}_2\text{O}_2\text{N}_2\cdot\text{Eu}$ ,  $\text{Ca}_{0.5}\text{Zn}_{0.5}\text{Si}_2\text{O}_2\text{N}_2\cdot\text{Eu}$ ,  $\text{Ca}_{0.5}\text{Be}_{0.5}\text{Si}_2\text{O}_2\text{N}_2\cdot\text{Eu}$ ,  $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Si}_2\text{O}_2\text{N}_2\cdot\text{Eu}$ ,  $\text{Ca}_{0.8}\text{Mg}_{0.2}\text{Si}_2\text{O}_2\text{N}_2\cdot\text{Eu}$ ,  $\text{Sr}_{0.8}\text{Mg}_{0.2}\text{Si}_2\text{O}_2\text{N}_2\cdot\text{Eu}$ ,  $\text{Ca}_{0.5}\text{Mg}_{0.5}\text{Si}_2\text{O}_2\text{N}_2\cdot\text{Eu}$ ,  $\text{Sr}_{0.5}\text{Mg}_{0.5}\text{Si}_2\text{O}_2\text{N}_2\cdot\text{Eu}$ ,  $\text{CaSi}_2\text{B}_{0.1}\text{O}_2\text{N}_2\cdot\text{Eu}$ ,  $\text{SrSi}_2\text{B}_{0.1}\text{O}_2\text{N}_2\cdot\text{Eu}$ ,  $\text{BaSi}_2\text{B}_{0.1}\text{O}_2\text{N}_2\cdot\text{Eu}$ ,  $\text{ZnSi}_2\text{B}_{0.1}\text{O}_2\text{N}_2\cdot\text{Eu}$ ,  $\text{CaGe}_2\text{B}_{0.01}\text{O}_2\text{N}_2\cdot\text{Eu}$ ,  $\text{SrGe}_2\text{B}_{0.01}\text{O}_2\text{N}_2\cdot\text{Eu}$ ,  $\text{BaGe}_2\text{B}_{0.01}\text{O}_2\text{N}_2\cdot\text{Eu}$ ,  $\text{ZnGe}_2\text{B}_{0.01}\text{O}_2\text{N}_2\cdot\text{Eu}$ ,  $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{Si}_2\text{B}_{0.3}\text{O}_2\text{N}_2\cdot\text{Eu}$ ,  $\text{CaSi}_{2.5}\text{O}_{1.5}\text{N}_3\cdot\text{Eu}$ ,  $\text{SrSi}_{2.5}\text{O}_{1.5}\text{N}_3\cdot\text{Eu}$ ,  $\text{BaSi}_{2.5}\text{O}_{1.5}\text{N}_3\cdot\text{Eu}$ ,  $\text{Ca}_{0.5}\text{Ba}_{0.5}\text{Si}_{2.5}\text{O}_{1.5}\text{N}_3\cdot\text{Eu}$ ,  $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{Si}_{2.5}\text{O}_{1.5}\text{N}_3\cdot\text{Eu}$ ,  $\text{Ca}_{1.5}\text{Si}_{2.5}\text{O}_{2.5}\text{N}_{2.7}\cdot\text{Eu}$ ,  $\text{Sr}_{1.5}\text{Si}_{2.5}\text{O}_{2.5}\text{N}_{2.7}\cdot\text{Eu}$ ,  $\text{Ba}_{1.5}\text{Si}_{2.5}\text{O}_{2.5}\text{N}_{2.7}\cdot\text{Eu}$ ,  $\text{Ca}_{1.0}\text{Ba}_{0.5}\text{Si}_{2.5}\text{O}_{1.5}\text{N}_3\cdot\text{Eu}$ ,  $\text{Ca}_{1.0}\text{Sr}_{0.5}\text{Si}_{2.5}\text{O}_{1.5}\text{N}_3\cdot\text{Eu}$ ,  $\text{Ca}_{0.5}\text{Si}_{1.5}\text{O}_{1.5}\text{N}_{1.7}\cdot\text{Eu}$ ,  $\text{Sr}_{0.5}\text{Si}_{1.5}\text{O}_{1.5}\text{N}_{1.7}\cdot\text{Eu}$ ,  $\text{Ba}_{0.5}\text{Si}_{1.5}\text{O}_{1.5}\text{N}_{1.7}\cdot\text{Eu}$ ,  $\text{Ca}_{0.3}\text{Ba}_{0.2}\text{Si}_{2.5}\text{O}_{1.5}\text{N}_3\cdot\text{Eu}$ ,  $\text{Ca}_{0.2}\text{Sr}_{0.3}\text{Si}_{2.5}\text{O}_{1.5}\text{N}_3\cdot\text{Eu}$  and the like can be used. Further, as shown here, the oxynitride phosphor of Embodiment 1 can change a ratio of O to N, and the color tone and brightness can be adjusted by changing the ratio. Further, a molar ratio of cation to anion which is shown by  $(L + M)/(O + N)$  can be also changed, and the luminescence spectrum and intensity can be finely adjusted thereby. This can be carried out, for example, by carrying out treatment such as vacuum and removing N and O, but the present invention is not limited to this process. In the composition of the oxynitride phosphor, there may be contained at least one or more of Li, Na, K, Rb, Cs, Mn, Re, Cu, Ag and Au, and the brightness and luminescence efficiency such as quantum efficiency can be adjusted by adding these. Further, other elements may be



contained so far as the properties are not damaged.

[0038]

L is at least one or more of Group II elements selected from the group consisting of Mg, Ca, Sr, Ba and Zn. That is, L may be single bodies such as Ca and Sr, and may comprise the combination of a plural number of elements such as Ca and Sr, Ca and Ba, Sr and Ba, and Ca and Mg. Further, when L is the combination of plural number of elements, the composition ratio can be varied. For example, the compounding ratio can be varied for the mixture of Sr and Ca, if necessary.

[0039]

M is at least one or more of Group IV elements selected from the group consisting of C, Si, Ge, Sn, Ti, Zr and Hf. M may be also single bodies such as Si and Ge, and may comprise the combination of a plural number of elements such as Si and Ge, and Si and C. In the present invention, the above-mentioned Group IV elements can be used but Si and Ge are preferably used. The phosphor having good crystallinity and low cost can be provided using Si and Ge.

[0040]

R is rare earth elements. Specifically, R is one or 2 or more elements selected from La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu. In the present invention, Eu is preferably used among these rare earth elements. Further, Eu and at least one or more elements selected from rare earth elements may be contained. Eu is preferably contained by 70% by weight or more as R.

[0041]

Europium Eu being the rare earth elements is used as a luminescence center. The present specification, the phosphor using Eu being a typical example as the luminescence center is occasionally illustrated, but the present invention is not limited to this. Europium has mainly a divalent and trivalent energy levels. The phosphor of Embodiment 1 uses  $\text{Eu}^{2+}$  as the activator for an alkali earth metal silicone nitride being the mother body.  $\text{Eu}^{2+}$  is easily oxidized and commercially available as the composition of

Eu<sub>2</sub>O<sub>3</sub> in general.

[0042]

L and M of the main components can be also used as compounds thereof as the mother material. These L and M of the main components can be used as metals, oxides, imides, amides, nitrides, and various salts. Further, the elements of L and M of the main components may be preliminarily mixed to be used.

[0043]

Q is at least one or more of Group III elements selected from the group consisting of B, Al, Ga and In. Q is also used as metals, oxides, imides, amides, nitrides, and various salts. For example, they are B<sub>2</sub>O<sub>6</sub>, H<sub>3</sub>BO<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, AlN, GaCl<sub>3</sub>, InCl<sub>3</sub> and the like.

[0044]

The nitride of L, the nitride of M and the oxide of M are mixed as the mother body materials. The oxide of Eu is mixed with said mother body materials as the activator. These are weighed so as to be the desired phosphor composition, and mixed until being homogeneous. In particular, the nitride of L, the nitride of M and the oxide of M in the mother body materials are preferably mixed at molar ratios of  $0.5 < \text{the nitride of L} < 1.5$ ,  $0.25 < \text{the nitride of M} < 1.75$ , and  $2.25 < \text{the oxide of M} < 3.75$ . The oxynitride phosphor having a high brightness can be provided by mixing the nitride of L, the nitride of M and the oxide of M at afore mentioned molar ratios. Namely, the fixed amounts of these mother body materials are weighed and mixed so as to be the composition ratio of  $L_xM_yO_zN_{((2/3)X+Y-(2/3)Z-\omega)} \cdot R$  or  $L_xM_yQ_tO_zN_{((2/3)X+Y+T-(2/3)Z-\omega)} \cdot R$ .

[0045]

(Production process of oxynitride phosphor)

Then, the production process of the oxynitride phosphor related to the present invention, CaSi<sub>2</sub>O<sub>2</sub>N<sub>2</sub>:Eu is illustrated. The present invention is not limited to the production processes below.

[0046]

The nitride of Ca, the nitride of Si, the oxide of Si and the oxide of Eu are mixed.

[0047]

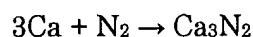
Firstly, the nitride of Ca, the nitride of Si, the oxide of Si and the oxide of Eu are prepared. As these raw materials, those purified are preferably used, but those commercially available may be used. Firstly, Ca of a raw material is crushed. The Ca of a raw material is preferably used as a single body, but compounds such as an imide compound, an amide compound and CaO can be also used. Further, the Ca of a raw material may be those containing B, Ga and the like. The crushing of the Ca of a raw material is carried out in a globe box in argon atmosphere. It is preferable that the mean particle diameter of Ca obtained by the crushing is about 0.1 $\mu$ m to 15 $\mu$ m, but is not limited to this range. The purity of Ca is preferably 2N or more, but is not limited to this range.

[0048]

Ca of a raw material is nitrified in nitrogen atmosphere. The reaction is shown in Formula 1.

[0049]

[Formula 1]



The nitride of Ca can be obtained by nitrifying the Ca crushed at a temperature of 600 to 900°C for about 5 hours in nitrogen atmosphere. As the nitride of Ca, it is needless to say that those with high purity are preferable. As the nitride of Ca, those commercially available can be also used.

[0050]

Then the nitride of Ca is crushed. The crushing of the nitride of Ca is carried out in a globe box in argon atmosphere or in nitrogen atmosphere.

[0051]

Si of a raw material is crushed. The Si of a raw material is preferably used as a single body, but a nitride compound, an imide compound, an amide compound and the like can be also used. For example, they are Si<sub>3</sub>N<sub>4</sub>, Si(NH<sub>2</sub>)<sub>2</sub>, Mg<sub>2</sub>Si, Ca<sub>2</sub>Si, SiC and the like.

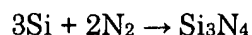
The purity of the Si of a raw material is preferably 3N or more, but B, Ga and the like may be contained. The crushing of Si of a raw material is carried out in a globe box in argon atmosphere or in nitrogen atmosphere, in like manner as the Ca of a raw material. It is preferable that the mean particle diameter of the Si compound is about 0.1µm to 15µm.

[0052]

The Si of a raw material is nitrified in nitrogen atmosphere. The reaction formula is shown in Formula 2.

[0053]

[Formula 2]



Silicon, Si is also nitrified at a temperature of 800 to 1200°C for about 5 hours in nitrogen atmosphere to obtain silicon nitride. It is needless to say that the silicon nitride used in the present invention is preferably those having high purity. Further, those which are commercially available can be also used.

[0054]

Then, the nitride of Si is crushed.

[0055]

As SiO<sub>2</sub> being the oxide of Si, those which are commercially available are used (Silicon Dioxide 99.9%, 190-09072, manufactured by Wako Pure Chemicals Industries, Ltd.).

[0056]

Raw materials which were purified or produced as above are weighed so as to be a fixed molar amount. The weighted raw materials are mixed.

[0057]

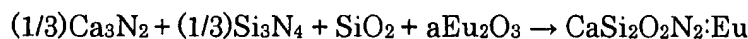
Then, the mixture of the nitride of Ca, the nitride of Si, the oxide of Si, and the oxide of Eu is calcined at about 1500°C in ammonia atmosphere. The calcined mixture is charged in a crucible to be calcined.

[0058]

The oxynitride phosphor represented by  $\text{CaSi}_2\text{O}_2\text{N}_2\cdot\text{Eu}$  can be obtained by mixing and calcination. The reaction formula of the basic constituting elements by the calcination is shown in Formula 3.

[0059]

[Formula 3]



[0060]

However, the composition is a typical composition deduced from the compounding ratio, and has adequate properties which are worthwhile for practical use, around the ratio. Further, the composition of the objective phosphors can be changed by changing the compounding ratio of the respective raw materials.

[0061]

The calcination can use a tube furnace, a small size furnace, a high frequency furnace and a metal furnace and the like. The calcination temperature is not specifically limited. The calcination is preferably carried out at a temperature of 1200 to 1700°C, and a calcination temperature of 1400 to 1700°C is more preferable. It is preferable to carry out the calcination of the raw materials of the phosphor using a crucible made of boron nitride (BN) material and a boat. A crucible made of alumina ( $\text{Al}_2\text{O}_3$ ) material can be also used in addition to the crucible made of boron nitride material.

[0062]

Further, reductive atmosphere is inactive gas atmospheres such as nitrogen atmosphere, nitrogen-hydrogen atmosphere, ammonia atmosphere and argon atmosphere, etc.

[0063]

The objective oxynitride phosphor can be obtained by using the above production process.

[0064]

Further, the oxynitride phosphor represented by  $\text{Ca}_x\text{Si}_y\text{B}_t\text{O}_z\text{N}_{((2/3)X+Y+T-(2/3)Z-\omega)}\cdot\text{Eu}$

which contains B can be produced as below.

[0065]

A B compound,  $\text{H}_3\text{BO}_3$  is preliminarily mixed with the oxide of Eu in dry condition. Europium oxide is used as the Eu compound, but metal europium, europium nitride and the like can be also used in like manner as the fore-mentioned other constitution elements. Additionally, an imide compound, a amide compound and the like can be used as the Eu compound. Europium oxide is preferably those having high purity, but those commercially available can be also used. A B compound is mixed in a dry process but a wet mixing can be also carried out.

[0066]

The production process of the oxynitride phosphor is illustrated exemplifying the B compound  $\text{H}_3\text{BO}_3$ . However, there are Li, K, Na and the like as the component constituting elements other than B, and as these compounds, for example, there can be used  $\text{LiOH} \cdot \text{H}_2\text{O}$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{K}_2\text{CO}_3$ ,  $\text{RbCl}$ ,  $\text{CsCl}$ ,  $\text{Mg}(\text{NO}_3)_2$ ,  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{TiOSO}_4 \cdot \text{H}_2\text{O}$ ,  $\text{ZrO}(\text{NO}_3)_2$ ,  $\text{HfCl}_4$ ,  $\text{MnO}_2$ ,  $\text{ReCl}_5$ ,  $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ ,  $\text{AgNO}_3$ ,  $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ ,  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{GeO}_2$ ,  $\text{Sn}(\text{CH}_3\text{COO})_2$  and the like.

[0067]

A mixture of Eu and B is crushed. The mean particle diameter of the mixture of Eu and B after the crushing is preferably about  $0.1\mu\text{m}$  to  $15\mu\text{m}$ .

[0068]

After the above-mentioned crushing, the nitride of Ca, the nitride of Si, the oxide of Si, and the oxide of Eu containing B are mixed in like manner as the fore-mentioned production steps of  $\text{CaSi}_2\text{O}_2\text{N}_2\text{:Eu}$ . After said mixing, calcination is carried out and the objective oxynitride phosphor can be obtained.

[0069]

[EXAMPLE]

<Examples 1 to 5>

Table 1 shows the properties of the oxynitride phosphors of Examples 1 to 5

related to the present invention.

[0070]

Further, Fig. 1 is a chart showing luminescence spectra when the nitride phosphors of Examples 1 to 5 were excited at  $\text{Ex} = 400\text{nm}$ . Fig. 2 is a chart showing the luminescence spectra when the oxynitride phosphors of Examples 1 to 5 were excited at  $\text{Ex} = 460\text{nm}$ . Fig. 3 is a chart showing the excitation spectra of the oxynitride phosphors of Examples 1 to 5. Fig. 4 is a chart showing the reflection spectra of the oxynitride phosphors of Examples 1 to 5. Fig. 5 is an SEM (scanning electron microscope) photographing the oxynitride phosphor of Example 1. Hereat, the name of a color and chromaticity are according to JIS Z8110.

[0071]

Table 1

	Ex=400nm			
	Color tone X	Color tone Y	Peak wavelength (nm)	
Example 1	0.434	0.543	561	3.5
Example 2	0.433	0.543	561	4.0
Example 3	0.349	0.608	539	4.0
Example 4	0.352	0.604	539	3.5
Example 5	0.182	0.55	509	3.5

	Ex=460nm		
	Color tone X	Color tone Y	Peak wavelength (nm)
Example 1	0.437	0.545	564
Example 2	0.434	0.546	564
Example 3	0.347	0.616	540
Example 4	0.351	0.614	540
Example 5	0.214	0.623	510

[0072]

Example 1 is the oxynitride phosphor represented by  $\text{CaSi}_2\text{O}_2\text{N}_2\cdot\text{Eu}$ . Example 2 is the oxynitride phosphor represented by  $\text{Ca}_{0.90}\text{Mg}_{0.10}\text{Si}_2\text{O}_2\text{N}_2\cdot\text{Eu}$ . Example 3 is the oxynitride phosphor represented by  $\text{SrSi}_2\text{O}_2\text{N}_2\cdot\text{Eu}$ . Example 4 is the oxynitride phosphor represented by  $\text{Sr}_{0.90}\text{Mg}_{0.10}\text{Si}_2\text{O}_2\text{N}_2\cdot\text{Eu}$ . Example 5 is the oxynitride phosphor represented

by  $\text{BaSi}_2\text{O}_2\text{N}_2\cdot\text{Eu}$ .

[0073]

$\text{Ca}_3\text{N}_2$ ,  $\text{Si}_3\text{N}_4$ ,  $\text{SiO}_2$  and  $\text{Eu}_2\text{O}_3$  were used as the raw materials. The raw materials are crushed to 0.1 to 3.0 $\mu\text{m}$ . After crushing following raw materials are used in the Example 1.

$\text{Ca}_3\text{N}_2$  : 6.01 g

$\text{Si}_3\text{N}_4$  : 5.99 g

$\text{SiO}_2$  : 7.36 g

$\text{Eu}_2\text{O}_3$  : 0.66 g

After weighing the above-mentioned amounts,  $\text{Ca}_3\text{N}_2$ ,  $\text{Si}_3\text{N}_4$ ,  $\text{SiO}_2$  and  $\text{Eu}_2\text{O}_3$  were mixed under nitrogen atmosphere in a glove box until uniformity. The concentration of Eu is 0.43% by mol in Examples 1 to 5.

[0074]

In Example 1, the mix ratio (molar ratio) of the raw materials is  $\text{Ca}_3\text{N}_2$  :  $\text{Si}_3\text{N}_4$  :  $\text{SiO}_2$  :  $\text{Eu}_2\text{O}_3$  = 1 : 0.51 : 3.02 : 0.046. 6.01g of  $\text{Ca}_3\text{N}_2$  (molecular weight = 148.3), 5.99g of  $\text{Si}_3\text{N}_4$  (molecular weight = 140.3), 7.36g of  $\text{SiO}_2$  (molecular weight = 60.09) and 0.66g of  $\text{Eu}_2\text{O}_3$  (molecular weight = 352.0) were weighed so as to be the mixing ratio, and mixed.

[0075]

The above-mentioned compounds were mixed, the mixture was charged in a boron nitride crucible in ammonia atmosphere, and calcination was carried out at about 1500°C for about 5 hours.

[0076]

The objective oxynitride phosphor was obtained thereby. The theoretical composition of the oxynitride phosphor obtained is  $\text{CaSi}_2\text{O}_2\text{N}_2\cdot\text{Eu}$ .

[0077]

When the % by weight of O and N in the oxynitride phosphor of Example 1 was measured, O and N were contained by 19.3% by weight and 14.5% by weight respectively. The weight ratio of O to N is O : N = 1 : 0.75.



[0078]

The calcination of the oxynitride phosphor related to Examples is carried out in ammonia atmosphere using a boron nitride crucible. A crucible made of a metal is not preferably used for the crucible. When the crucible made of a metal is used, it is considered that the crucible is eroded and it causes the lowering of luminescence properties. Accordingly, it is preferable to use a crucible made of ceramics such as alumina.

[0079]

Example 2 is the oxynitride phosphor in which the portion of Ca was substituted with Mg. Example 2 used magnesium nitride,  $\text{Mg}_3\text{N}_2$  (MG102PB 98%, manufactured by High Purity Chemicals Co.) (molecular weight = 101.0), and the under-mentioned amounts of crushed powders were weighed so that the mixing ratio (molar ratio) of the raw materials is  $\text{Ca}_3\text{N}_2 : \text{Mg}_3\text{N}_2 : \text{Si}_3\text{N}_4 : \text{SiO}_2 : \text{Eu}_2\text{O}_3 = 1 : 0.12 : 0.57 : 3.37 : 0.052$ .

$\text{Ca}_3\text{N}_2$  : 5.44 g

$\text{Mg}_3\text{N}_2$  : 0.43 g

$\text{Si}_3\text{N}_4$  : 6.05 g

$\text{SiO}_2$  : 7.43 g

$\text{Eu}_2\text{O}_3$  : 0.67 g

Further, said raw materials were mixed and calcination was carried out under the same conditions as Example 1.

[0080]

Example 3 is the oxynitride phosphor in which Ca of Example 1 was substituted with Sr. Example 3 used strontium nitride,  $\text{Sr}_3\text{N}_4$  (molecular weight = 290.9), and the under-mentioned amounts of crushed powders were weighed so that the mixing ratio (molar ratio) of the raw materials is  $\text{Sr}_3\text{N}_2 : \text{Si}_3\text{N}_4 : \text{SiO}_2 : \text{Eu}_2\text{O}_3 = 1 : 0.51 : 3.02 : 0.046$ .

$\text{Sr}_3\text{N}_2$  : 9.14 g

$\text{Si}_3\text{N}_4$  : 4.65 g

$\text{SiO}_2$  : 5.71 g

$\text{Eu}_2\text{O}_3$  : 0.51 g

Example 3 mixed said raw materials were mixed and carried out calcination under the same conditions as Example 1.

When the % by weight of O and N in the oxynitride phosphor of Example 3 was measured, O and N were contained by 15.3% by weight and 11.2% by weight respectively in the total amount. The weight ratio of O to N is  $O : N = 1 : 0.73$ .

[0081]

Example 4 is the oxynitride phosphor in which Ca of Example 2 was substituted with Sr. In Example 4, the under-mentioned amounts of crushed powders were weighed so that the mixing ratio (molar ratio) of the raw materials is  $Sr_3N_2 : Mg_3N_2 : Si_3N_4 : SiO_2 : Eu_2O_3 = 1 : 0.12 : 0.57 : 3.37 : 0.052$ .

$Sr_3N_2 : 8.46 \text{ g}$

$Mg_3N_2 : 0.34 \text{ g}$

$Si_3N_4 : 4.80 \text{ g}$

$SiO_2 : 5.89 \text{ g}$

$Eu_2O_3 : 0.53 \text{ g}$

Said raw materials were mixed and calcination was carried out under the same conditions as Example 1.

[0082]

Example 5 is the oxynitride phosphor in which Ca of Example 1 was substituted with Ba. Example 5 used barium nitride,  $Ba_3N_2$  (molecular weight = 316.6), and the under-mentioned amounts of crushed powders were weighed so that the mixing ratio (molar ratio) of the raw materials is  $Ba_3N_2 : Si_3N_4 : SiO_2 : Eu_2O_3 = 1 : 0.76 : 0.22 : 0.033$ .

$Ba_3N_2 : 11.2 \text{ g}$

$Si_3N_4 : 3.77 \text{ g}$

$SiO_2 : 4.63 \text{ g}$

$Eu_2O_3 : 0.42 \text{ g}$

Said raw materials were mixed and calcination was carried out under the same conditions as Example 1.

[0083]

Any of the calcined products of Examples 1 to 5 is crystalline powder or particles. The particle diameter was about 1 to 5 $\mu$ m.

[0084]

The measurement of the excitation spectra of the oxynitride phosphors of Examples 1 to 5 was carried out. As a result of the measurement, they are strongly excited at a shorter wavelength side than 490nm.

[0085]

The oxynitride phosphors of Examples 1 to 5 were excited by  $E_x = 460\text{nm}$ . Since  $E_x = 460\text{nm}$  is a wavelength often used in a blue light-emitting element, excitation was carried out at said wavelength region. As a result, the oxynitride phosphor of Example 1 has a luminescence color at a yellow region of color tone,  $x = 0.437$  and color tone  $y = 0.545$ . The oxynitride phosphor of Example 4 has a luminescence color at a yellow region of color tone,  $x = 0.351$  and color tone,  $y = 0.614$ . Any of the oxynitride phosphors of Examples 1 to 5 exhibited higher luminescence efficiency than a conventional phosphor.

[0086]

The oxynitride phosphors of Examples 1 to 5 were excited by  $E_x = 400\text{nm}$ . The oxynitride phosphor of Example 1 has a luminescence color at a yellow green region of color tone,  $x = 0.434$  and color tone,  $y = 0.543$ . The oxynitride phosphor of Example 3 has a luminescence color at a yellow green region of color tone,  $x = 0.349$  and color tone,  $y = 0.608$ . Any of the oxynitride phosphors of Examples 1 to 5 exhibited higher luminescence efficiency than a conventional phosphor.

[0087]

Further, temperature properties were excellent. The temperature properties are shown by relative brightness in which luminescence brightness at 25°C is 100%. The particle diameter is a value according to an air transmission process called F.S.S.No. (Fisher Sub Sieve Sizer's No.). The temperature properties of Examples 1 to 5 are 95 to 100% at 100°C. They were 65 to 90% at 200°C.

[0088]

When the X-ray diffraction images of the above-mentioned these oxynitride phosphors were measured, any image shows a sharp diffraction peak, and it was cleared that the phosphors obtained were crystalline compounds having regularity.

[0089]

<Examples 6 to 15>

Table 2 shows the properties of Examples 6 to 15 of the oxynitride phosphors related to the present invention.

[0090]

Further, Fig. 6 is a chart showing the luminescence spectra when the oxynitride phosphors of Examples 6 to 10 were excited at  $E_x = 400\text{nm}$ . Fig. 7 is a chart showing the luminescence spectra when the oxynitride phosphors of Examples 6 to 10 were excited at  $E_x = 460\text{nm}$ . Fig. 8 is a chart showing the luminescence spectra when the oxynitride phosphors of Examples 11 to 15 were excited at  $E_x = 400\text{nm}$ . Fig. 9 is a chart showing the luminescence spectra when the oxynitride phosphors of Examples 11 to 15 were excited at  $E_x = 460\text{nm}$ . Fig. 10 is a chart showing the excitation spectra of the oxynitride phosphors of Examples 11 to 15. Fig. 11 is a chart showing the reflection spectra of the oxynitride phosphors of Examples 11 to 15.

[0091]

Table 2

Excitation at $E_x = 400\text{ nm}$						
	Sr/Ca	Luminescence peak wavelength	Color tone	Color tone	Luminescence brightness	Quantum efficiency
	Molar ratio	(nm)	x	y	(%)	(%)
Example 6	0/10	561	0.434	0.543	100.0	100.0
Example 7	3/7	543	0.388	0.570	111.0	106.3
Example 8	5/5	546	0.375	0.579	135.9	128.6
Example 9	7/3	544	0.372	0.593	148.0	131.8
Example 10	10/0	539	0.349	0.608	145.8	127.3

Excitation at Ex = 460 nm						
	Sr/Ca	Luminescence peak wavelength	Color tone	Color tone	Luminescence brightness	Quantum efficiency
	Molar ratio	(nm)	x	y	(%)	(%)
Example 6	0/10	564	0.437	0.545	100.0	100.0
Example 7	3/7	549	0.391	0.578	109.4	103.1
Example 8	5/5	545	0.378	0.588	125.4	116.9
Example 9	7/3	545	0.371	0.600	162.8	142.7
Example 10	10/0	540	0.347	0.616	138.8	119.2

Excitation at Ex = 400 nm						
	Sr/Ca	Luminescence peak wavelength	Color tone	Color tone	Luminescence brightness	Quantum efficiency
	Molar ratio	(nm)	x	y	(%)	(%)
Example 11	6/4	542	0.366	0.593	124.4	128.1
Example 12	7/3	541	0.366	0.595	133.3	135.8
Example 13	8/2	542	0.363	0.599	142.0	143.4
Example 14	9/1	540	0.353	0.605	122.7	123.2
Example 15	10/0	540	0.342	0.611	100.0	100.0

Excitation at Ex = 460 nm						
	Sr/Ca	Luminescence peak wavelength	Color tone	Color tone	Luminescence brightness	Quantum efficiency
	Molar ratio	(nm)	x	y	(%)	(%)
Example 11	6/4	542	0.365	0.603	134.5	137.8
Example 12	7/3	542	0.364	0.605	148.5	151.1
Example 13	8/2	542	0.360	0.609	156.8	158.4
Example 14	9/1	541	0.351	0.615	125.9	126.8
Example 15	10/0	539	0.339	0.622	100.0	100.0

[0092]

Examples 6 to 10 are the oxynitride phosphors represented by  $\text{Sr}_x\text{Ca}_{(1-x)}\text{Si}_2\text{O}_2\text{N}_2:\text{Eu}$  ( $0 \leq x \leq 1$ ), and carry out production changing a molar ratio of Sr to Ca.

[0093]

Examples 6 to 10 carried out the production of the oxynitride phosphors under almost the same condition as Example 1.  $\text{Sr}_3\text{N}_2$ ,  $\text{Ca}_3\text{N}_2$ ,  $\text{Si}_3\text{N}_4$ ,  $\text{SiO}_2$  and  $\text{Eu}_2\text{O}_3$  were used as raw materials. After weighing the fixed amounts of said raw materials,  $\text{Sr}_3\text{N}_2$ ,  $\text{Ca}_3\text{N}_2$ ,

Si<sub>3</sub>N<sub>4</sub>, SiO<sub>2</sub> and Eu<sub>2</sub>O<sub>3</sub> were mixed under nitrogen atmosphere in a glove box until uniformity. The concentration of Eu is 0.43% by mol in Examples 6 to 15.

[0094]

The above-mentioned compounds were mixed, the mixture was charged in a boron nitride crucible in ammonia atmosphere, and calcination was carried out at about 1450°C for about 5 hours.

[0095]

The objective oxynitride phosphor was obtained thereby.

[0096]

The luminescence brightness and quantum efficiency of Examples 6 to 10 are represented with a relative value on the basis of Example 6.

[0097]

From this result, when Examples 6 to 10 are excited by a light source nearby 400nm, the phosphors mixing Sr and Ca exhibited higher luminescence brightness and quantum efficiency than those using only Ca. On the other hand, when Example 6 to 10 are excited by a light source nearby 460nm, the phosphor of Sr : Ca = 7 : 3 exhibited the highest luminescence efficiency. Further, the luminescence efficiency can be improved by substituting the portion of Ca and increasing Sr. Further, the color tone can be changed by changing a molar ratio of Sr to Ca.

[0098]

Examples 11 to 15 are the oxynitride phosphors represented by Sr<sub>x</sub>Ca<sub>(10-x)</sub>Si<sub>2</sub>O<sub>2</sub>N<sub>2</sub>:Eu (0 ≤ X ≤ 1), and carry out production changing a molar ratio of Sr to Ca.

[0099]

Examples 11 to 15 carried out the production of the oxynitride phosphors under almost the same condition as Example 1. Sr<sub>3</sub>N<sub>2</sub>, Ca<sub>3</sub>N<sub>2</sub>, Si<sub>3</sub>N<sub>4</sub>, SiO<sub>2</sub> and Eu<sub>2</sub>O<sub>3</sub> were used as raw materials. After weighing the fixed amounts of said raw materials, Sr<sub>3</sub>N<sub>2</sub>, Ca<sub>3</sub>N<sub>2</sub>, Si<sub>3</sub>N<sub>4</sub>, SiO<sub>2</sub> and Eu<sub>2</sub>O<sub>3</sub> were mixed under nitrogen atmosphere in a glove box until

uniformity. The concentration of Eu is 0.43% by mol in Examples 6 to 15.

[0100]

The above-mentioned compounds were mixed, the mixture was charged in a boron nitride crucible in ammonia atmosphere, and calcination was carried out at about 1550°C for about 5 hours.

[0101]

The objective oxynitride phosphor was obtained thereby.

[0102]

The luminescence brightness and quantum efficiency of Examples 11 to 15 are represented with a relative value on the basis of Example 15.

[0103]

From this result, when Examples 11 to 15 are excited by a light source nearby 400nm, the phosphors mixing Sr and Ca exhibited higher luminescence brightness and quantum efficiency than those using only Sr. Further, when a molar ratio of Sr : Ca is Sr : Ca = 6 : 4 to 9 : 1, the luminescence efficiency can be improved. In particular, the high values of luminescence brightness and quantum efficiency are exhibited in case of Sr : Ca = 7 : 3 to 8 : 2. Further, the color tone can be changed by changing the molar ratio of Sr to Ca.

[0104]

<Examples 16 to 20>

Table 3 shows the properties of Examples 10, 16 to 20 of the oxynitride phosphors related to the present invention.

[0105]

Further, Fig. 12 is a chart showing the luminescence spectra when the oxynitride phosphors of Examples 10 and 16 to 20 were excited at  $\lambda_{\text{ex}} = 400\text{nm}$ . Fig. 13 is a chart showing the luminescence spectra when the oxynitride phosphors of Examples 10 and 16 to 20 were excited at  $\lambda_{\text{ex}} = 460\text{nm}$ . Fig. 14 is a chart showing the excitation spectra of the oxynitride phosphors of Examples 10 and 16 to 20. Fig. 15 is a chart showing the

reflection spectra of the oxynitride phosphors of Examples 10 and 16 to 20.

[0106]

Table 3

Excitation at Ex = 400 nm						
	Sr/Ba	Luminescence peak wavelength	Color tone	Color tone	Luminescence brightness	Quantum efficiency
	Molar ratio	(nm)	x	y	(%)	(%)
Example 10	10/0	539	0.349	0.608	100.0	100.0
Example 16	8/2	549	0.388	0.581	84.3	86.6
Example 17	6/4	556	0.404	0.556	77.5	83.2
Example 18	4/6	553	0.411	0.552	36.1	40.9
Example 19	2/8	524	0.269	0.595	19.9	22.5
Example 20	0/10	496	0.142	0.464	25.9	45.8

Excitation at Ex = 460 nm						
	Sr/Ba	Luminescence peak wavelength	Color tone	Color tone	Luminescence brightness	Quantum efficiency
	Molar ratio	(nm)	x	y	(%)	(%)
Example 10	10/0	540	0.347	0.616	100.0	100.0
Example 16	8/2	548	0.386	0.590	95.8	97.8
Example 17	6/4	558	0.408	0.571	87.6	92.7
Example 18	4/6	558	0.417	0.559	47.4	53.5
Example 19	2/8	527	0.293	0.621	13.6	15.2
Example 20	0/10	497	0.120	0.532	37.8	64.2

[0107]

Examples 10, 16 to 20 are the oxynitride phosphors represented by  $\text{Sr}_x\text{Ba}_{(1-x)}\text{Si}_2\text{O}_2\text{N}_2\cdot\text{Eu}$  ( $0 \leq x \leq 1$ ), and carry out production changing a molar ratio of Sr to Ba.

[0108]

Examples 10, 16 to 20 carried out the production of the oxynitride phosphors under almost the same condition as Example 1.  $\text{Sr}_3\text{N}_2$ ,  $\text{Ba}_3\text{N}_2$ ,  $\text{Si}_3\text{N}_4$ ,  $\text{SiO}_2$  and  $\text{Eu}_2\text{O}_3$  were used as raw materials. After weighing the fixed amounts of said raw materials,  $\text{Sr}_3\text{N}_2$ ,  $\text{Ba}_3\text{N}_2$ ,  $\text{Si}_3\text{N}_4$ ,  $\text{SiO}_2$  and  $\text{Eu}_2\text{O}_3$  were mixed under nitrogen atmosphere in a glove box until uniformity. The concentration of Eu is 0.43% by mol in Examples 10, 16 to 20.



[0109]

The above-mentioned compounds were mixed, the mixture was charged in a boron nitride crucible in ammonia atmosphere, and calcination was carried out at about 1450°C for about 5 hours.

[0110]

The objective oxynitride phosphors were obtained thereby.

[0111]

The luminescence brightness and quantum efficiency of Examples 10, 16 to 20 are represented with a relative value on the basis of Example 10.

[0112]

From this result, when Examples 10, 16 to 20 are excited by a light source nearby 400 nm and 460 nm, the phosphors being mixed at Sr : Ba = 6 : 4 to 8 : 2 exhibited higher luminescence brightness and quantum efficiency than those being mixed at Sr : Ba = 2 : 8. Further, the luminescence efficiency can be improved by substituting the portion of Ba and increasing Sr. Further, the color tone can be changed by changing a molar ratio of Sr to Ba. Further, the  $\text{BaSi}_2\text{N}_2\text{O}_2\text{:Eu}$  of Example 20 has the luminescence peak wavelength nearby 496nm and exhibits the high luminescence efficiency. The color rendering of the white light-emitting device can be improved by using the oxynitride phosphor related to Example 20.

[0113]

<Examples 21 to 24>

Table 4 shows the properties of Examples 21 to 24 of the oxynitride phosphors related to the present invention.

[0114]

Further, Fig. 16 is a chart showing the luminescence spectra when the oxynitride phosphors of Examples 21 to 24 were excited at  $\lambda_{\text{ex}} = 400\text{nm}$ . Fig. 17 is a chart showing the luminescence spectra when the oxynitride phosphors of Examples 21 to 24 were excited at  $\lambda_{\text{ex}} = 460\text{nm}$ . Fig. 18 is a chart showing the excitation spectra of the oxynitride

phosphors of Examples 21 to 24. Fig. 19 is a chart showing the reflection spectra of the oxynitride phosphors of Examples 21 to 24.

[0115]

Table 4

Excitation at Ex = 400 nm						
	Ca/Ba	Luminescence peak wavelength	Color tone	Color tone	Luminescence brightness	Quantum efficiency
	Molar ratio	(nm)	x	y	(%)	(%)
Example 21	8/2	570	0.456	0.502	100.0	100.0
Example 22	6/4	593	0.508	0.462	54.5	63.2
Example 23	4/6	542	0.353	0.425	42.6	52.1
Example 24	2/8	493	0.254	0.389	56.4	69.2

Excitation at Ex = 460 nm						
	Ca/Ba	Luminescence peak wavelength	Color tone	Color tone	Luminescence brightness	Quantum efficiency
	Molar ratio	(nm)	x	y	(%)	(%)
Example 21	8/2	570	0.456	0.502	100.0	100.0
Example 22	6/4	593	0.508	0.462	54.5	63.2
Example 23	4/6	542	0.353	0.425	42.6	52.1
Example 24	2/8	493	0.254	0.389	56.4	69.2

[0116]

Examples 21 to 24 are the oxynitride phosphors represented by  $\text{Ca}_x\text{Ba}_{(1-x)}\text{Si}_2\text{O}_2\text{N}_2\cdot\text{Eu}$  ( $0 \leq X \leq 1$ ), and carry out production changing a molar ratio of Ca to Ba.

[0117]

Examples 21 to 24 carried out the production of the oxynitride phosphors under almost the same condition as Example 1.  $\text{Ca}_3\text{N}_2$ ,  $\text{Ba}_3\text{N}_2$ ,  $\text{Si}_3\text{N}_4$ ,  $\text{SiO}_2$  and  $\text{Eu}_2\text{O}_3$  were used as raw materials. After weighing the fixed amounts of said raw materials,  $\text{Ca}_3\text{N}_2$ ,  $\text{Ba}_3\text{N}_2$ ,  $\text{Si}_3\text{N}_4$ ,  $\text{SiO}_2$  and  $\text{Eu}_2\text{O}_3$  were mixed under nitrogen atmosphere in a glove box until uniformity. The concentration of Eu is 0.43% by mol in Examples 21 to 24.

[0118]

The above-mentioned compounds were mixed, the mixture was charged in a boron

nitride crucible in ammonia atmosphere, and calcination was carried out at about 1450°C for about 5 hours.

[0119]

The objective oxynitride phosphors were obtained thereby.

[0120]

The luminescence brightness and quantum efficiency of Examples 21 to 24 are represented with a relative value on the basis of Example 21.

[0121]

From this result, when Examples 21 to 24 are excited by a light source nearby 400nm, the phosphors being mixed at Ca : Ba = 8 : 2 exhibited higher luminescence brightness and quantum efficiency than those being mixed at Ca : Ba = 4 : 6. On the other hand, when Examples 21 to 24 are excited by a light source nearby 460nm, the phosphor being mixed at Ca : Ba = 8 : 2 exhibited the higher luminescence brightness and quantum efficiency than that being mixed at Ca : Ba = 2 : 8. Further, the color tone can be changed by changing the molar ratio of Ca to Ba.

[0122]

<Examples 25 to 27>

The structural analysis of the oxynitride phosphors of Examples 25 to 27 was carried out. The composition of Example 25 is  $\text{CaSi}_2\text{O}_2\text{N}_2$ . The composition of Example 26 is  $\text{SrSi}_2\text{O}_2\text{N}_2$ . The composition of Example 27 is  $\text{BaSi}_2\text{O}_2\text{N}_2$ . Fig. 22 is a schematic view showing the rhombic system. Fig. 23 is a chart showing the X-ray diffraction pattern of the oxynitride phosphor of Example 25. Fig. 24 is a chart showing the X-ray diffraction pattern of the oxynitride phosphor of Example 26. Fig. 25 is a chart showing the X-ray diffraction pattern of the oxynitride phosphor of Example 27.

[0123]

From this result, the unit lattice of crystals of the oxynitride phosphor is attributed to the rhombic system. The rhombic system is  $a \neq b \neq c$  and  $\alpha = \beta = \gamma = 90^\circ$ , and has 3 of mutually perpendicular diads or two symmetry planes which cross with the diad.

[0124]

[EFFECT OF THE INVENTION]

As described above, a phosphor which is efficiently excited by light in a range from near ultraviolet to a short wavelength side region of visible light from an excitation light source and has a luminescence color at a blue green to yellow region is provided by the present invention. The emission efficiency is higher than the phosphor in the prior art. Since the phosphor related to the present invention is formed in powder or particles, it is easily to be produced and processed. The oxynitride phosphors can be improved in emitting properties by changing a composition. In addition, the oxynitride phosphors are stable and excellent in temperature characteristic. Therefore, the oxynitride phosphors related to the present invention have excellent technical meanings.

[BRIEF DESCRIPTION OF DRAWING]

Fig. 1 is a chart showing the luminescence spectra when the oxynitride phosphors of Examples 1 to 5 were excited at  $\text{Ex} = 400\text{nm}$ ;

Fig. 2 is a chart showing the luminescence spectra when the oxynitride phosphors of Examples 1 to 5 were excited at  $\text{Ex} = 460\text{nm}$ ;

Fig. 3 is a chart showing the excitation spectra of the oxynitride phosphors of Examples 1 to 5;

Fig. 4 is a chart showing the reflection spectra of the oxynitride phosphors of Examples 1 to 5;

Fig. 5 is an SEM photo photographing the oxynitride phosphor of Example 1;

Fig. 6 is a chart showing the luminescence spectra when the oxynitride phosphors of Examples 6 to 10 were excited at  $\text{Ex} = 400\text{nm}$ ;

Fig. 7 is a chart showing the luminescence spectra when the oxynitride phosphors of Examples 6 to 10 were excited at  $\text{Ex} = 460\text{nm}$ ;

Fig. 8 is a chart showing the luminescence spectra when the oxynitride phosphors of Examples 11 to 15 were excited at  $\text{Ex} = 400\text{nm}$ ;

Fig. 9 is a chart showing the luminescence spectra when the oxynitride phosphors

of Examples 11 to 15 were excited at  $E_x = 460\text{nm}$ ;

Fig. 10 is a chart showing the excitation spectra of the oxynitride phosphors of Examples 11 to 15;

Fig. 11 is a chart showing the reflection spectra of the oxynitride phosphors of Examples 11 to 15;

Fig. 12 is a chart showing the luminescence spectra when the oxynitride phosphors of Examples 10 and 16 to 20 were excited at  $E_x = 400\text{nm}$ ;

Fig. 13 is a chart showing the luminescence spectra when the oxynitride phosphors of Examples 10 and 16 to 20 were excited at  $E_x = 460\text{nm}$ ;

Fig. 14 is a chart showing the excitation spectra of the oxynitride phosphors of Examples 10 and 16 to 20;

Fig. 15 is a chart showing the reflection spectra of the oxynitride phosphors of Examples 10 and 16 to 20;

Fig. 16 is a chart showing the luminescence spectra when the oxynitride phosphors of Examples 21 to 24 were excited at  $E_x = 400\text{nm}$ ;

Fig. 17 is a chart showing the luminescence spectra when the oxynitride phosphors of Examples 21 to 24 were excited at  $E_x = 460\text{nm}$ ;

Fig. 18 is a chart showing the excitation spectra of the oxynitride phosphors of Examples 21 to 24;

Fig. 19 is a chart showing the reflection spectra of the oxynitride phosphors of Examples 21 to 24;

Fig. 20 is a schematic view showing the rhombic system;

Fig. 21 is a chart showing the X-ray diffraction pattern of the oxynitride phosphor of Example 25;

Fig. 22 is a chart showing the X-ray diffraction pattern of the oxynitride phosphor of Example 26;

Fig. 23 is a chart showing the X-ray diffraction pattern of the oxynitride phosphor of Example 27.

Fig. 1

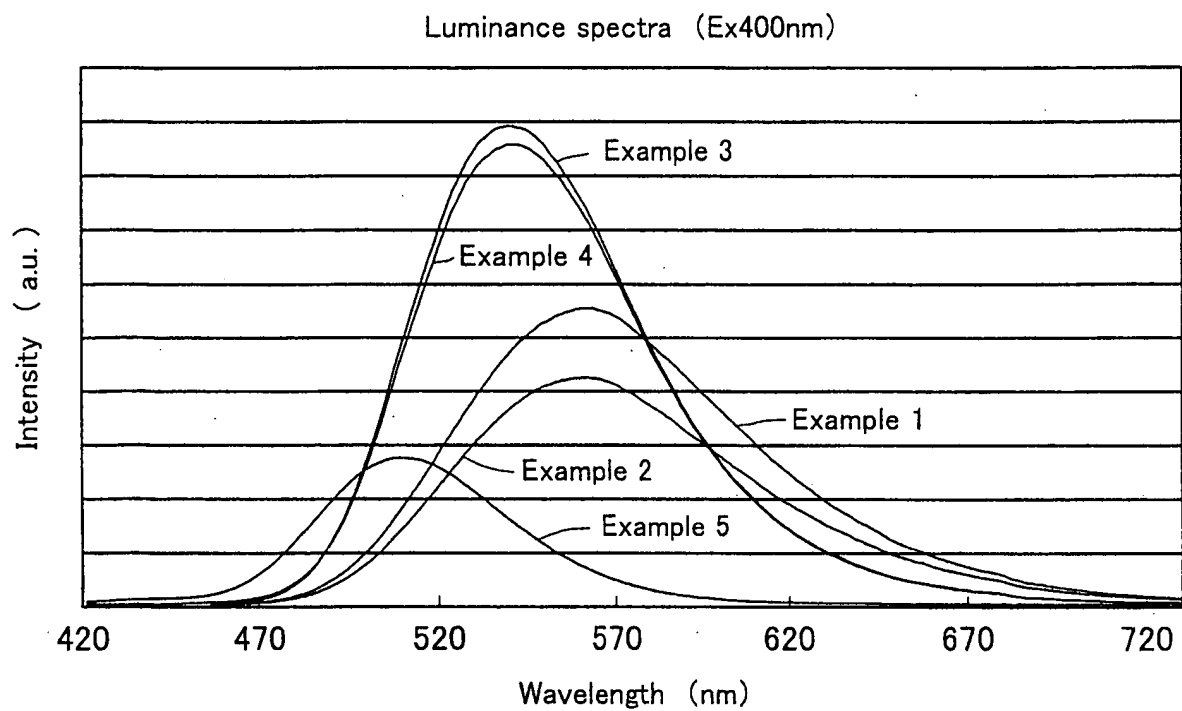


Fig. 2

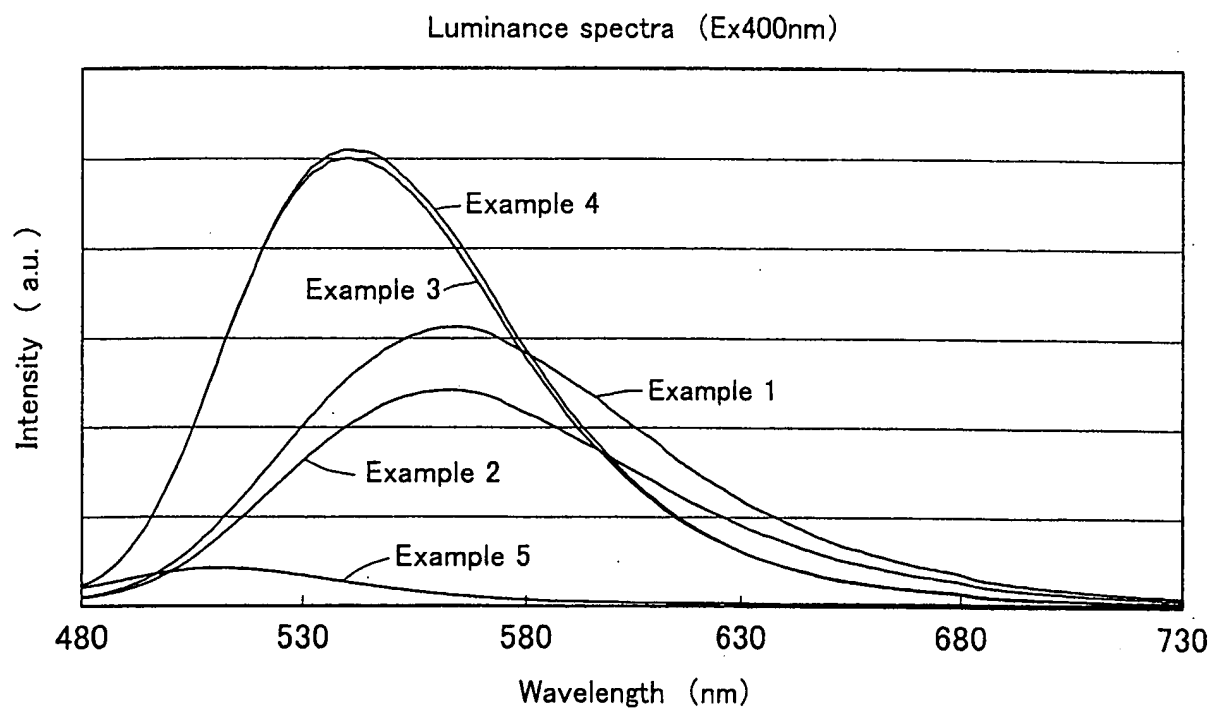


Fig. 3

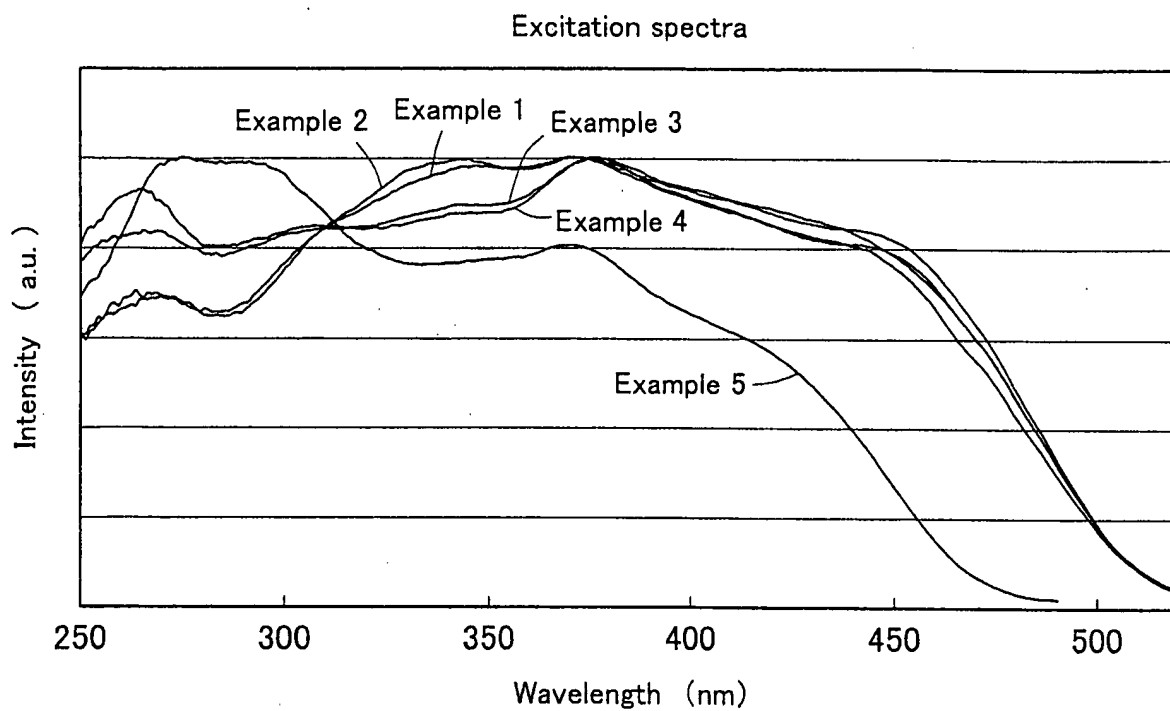


Fig. 4

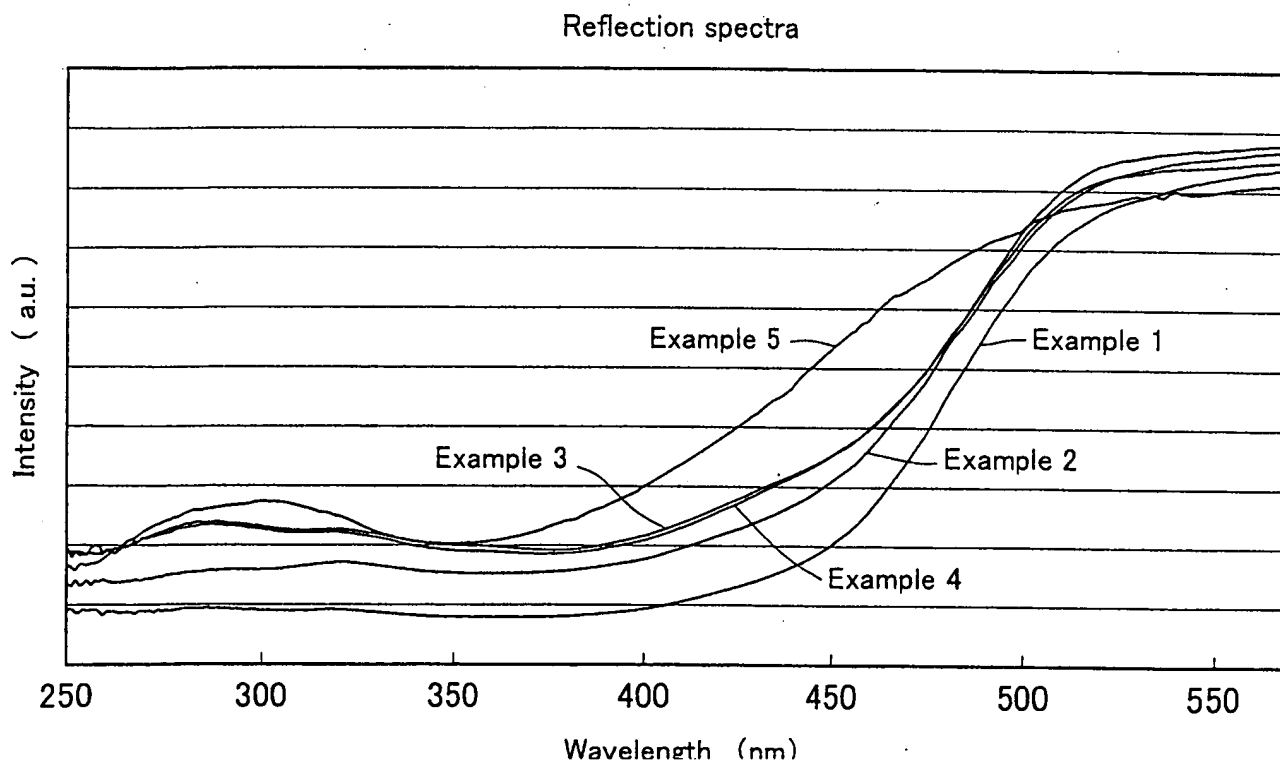
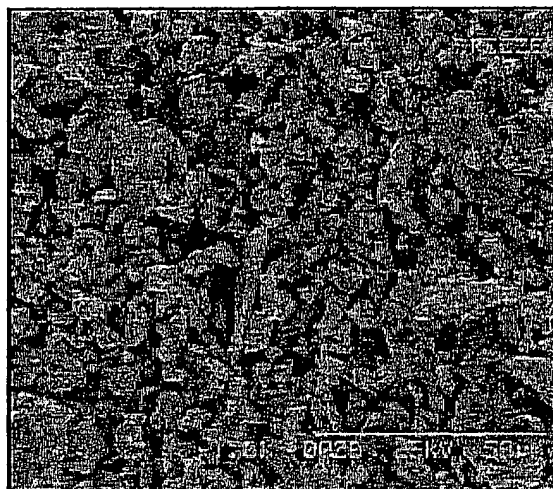


Fig. 5

(a)

×1000



(b)

×10000

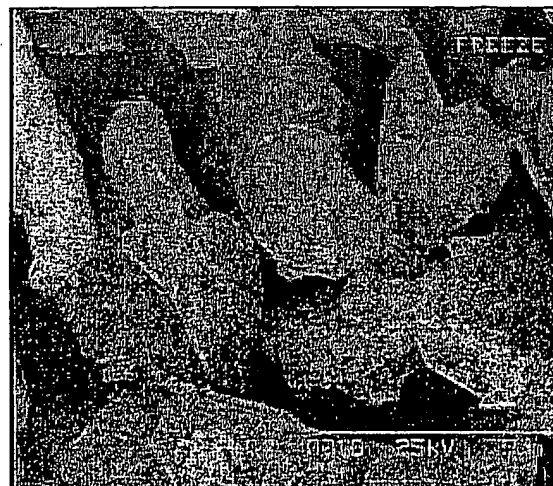




Fig. 6

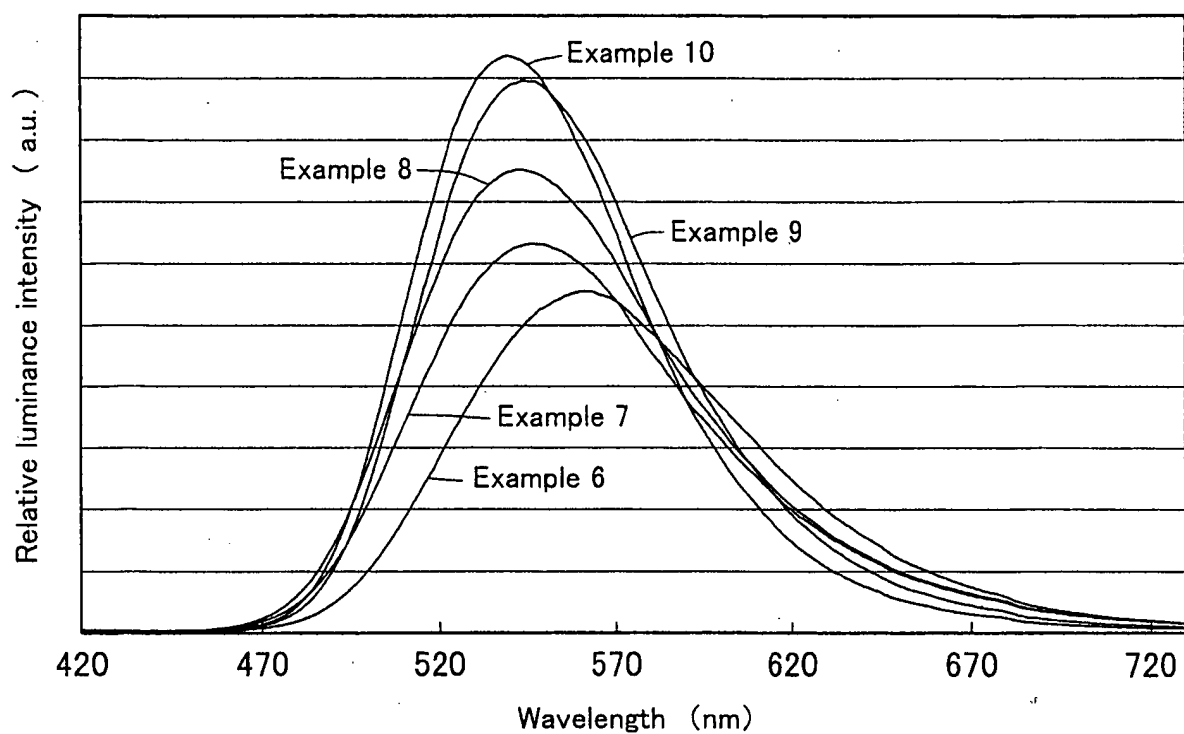


Fig. 7

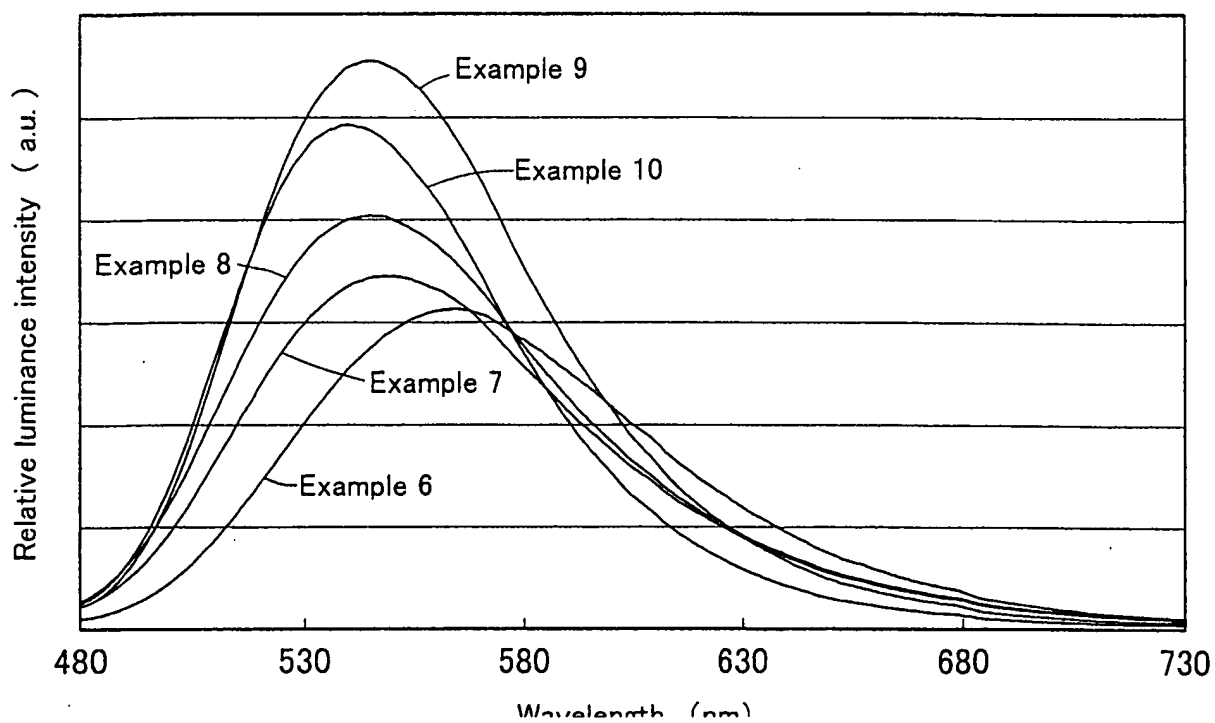


Fig. 8

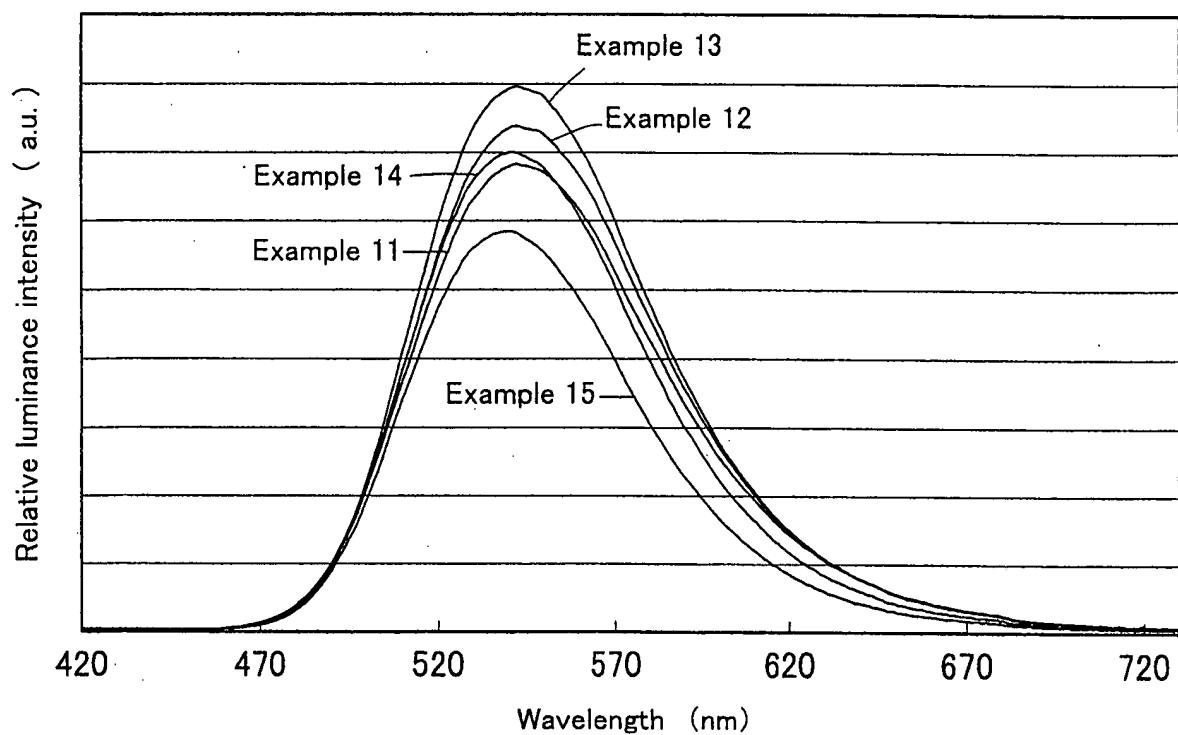


Fig. 9

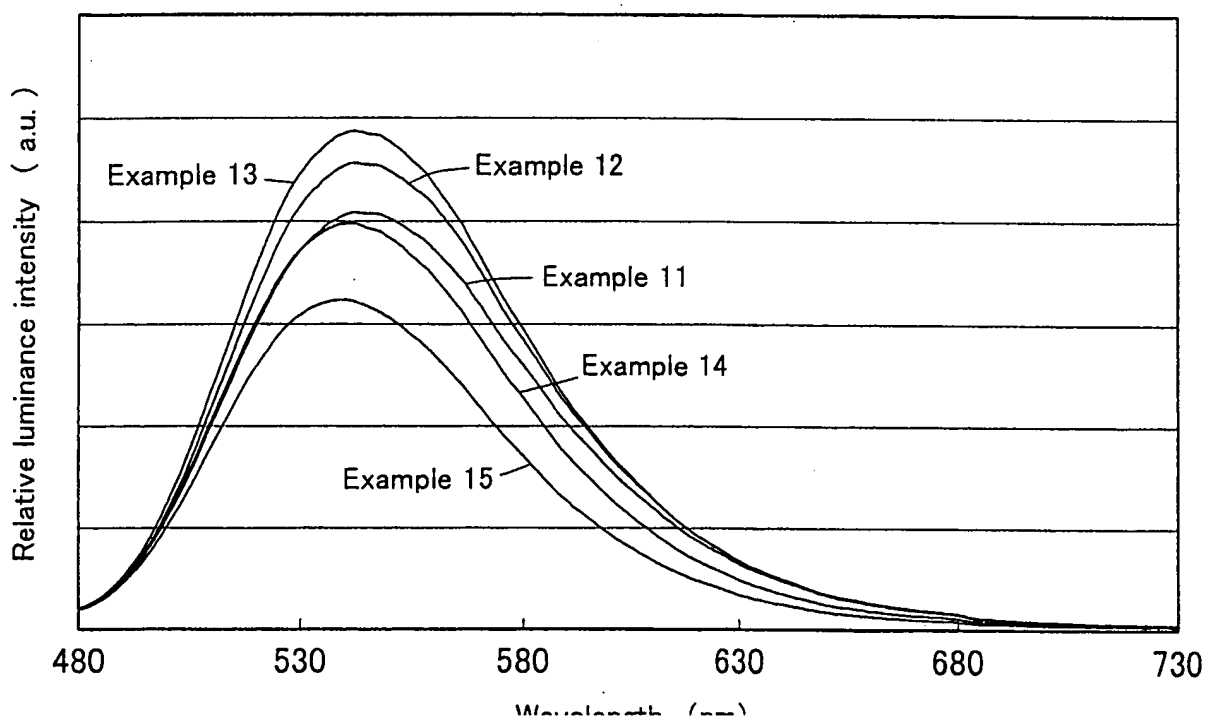


Fig. 10

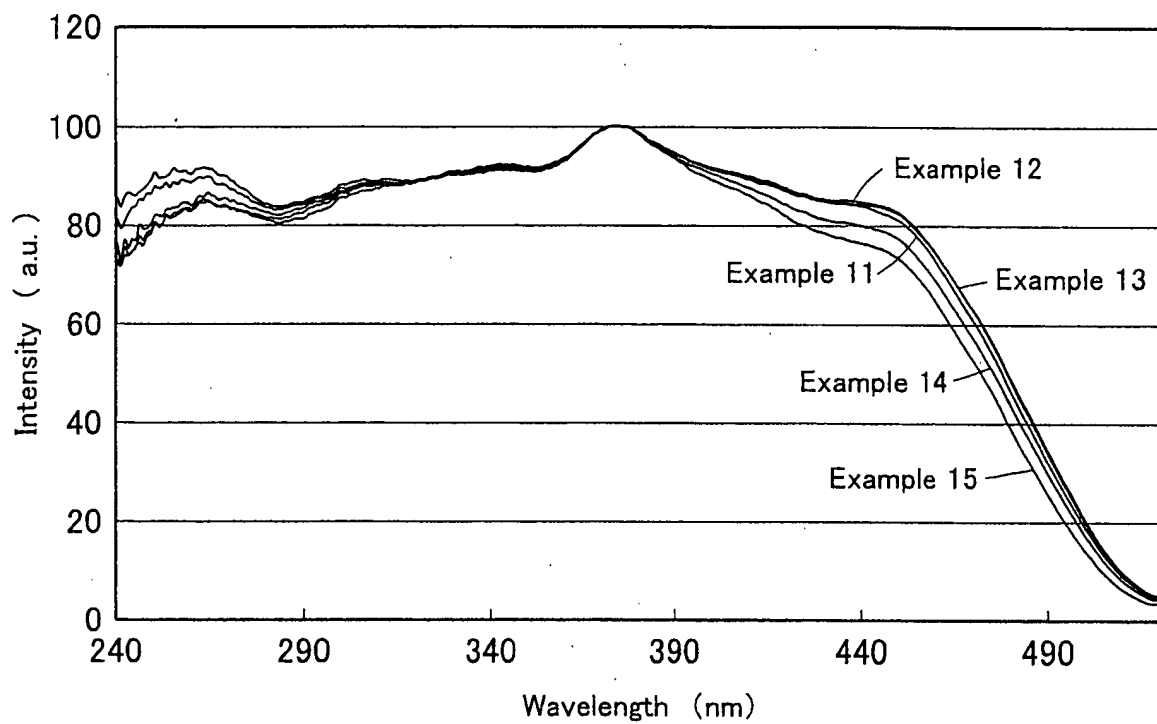


Fig. 11

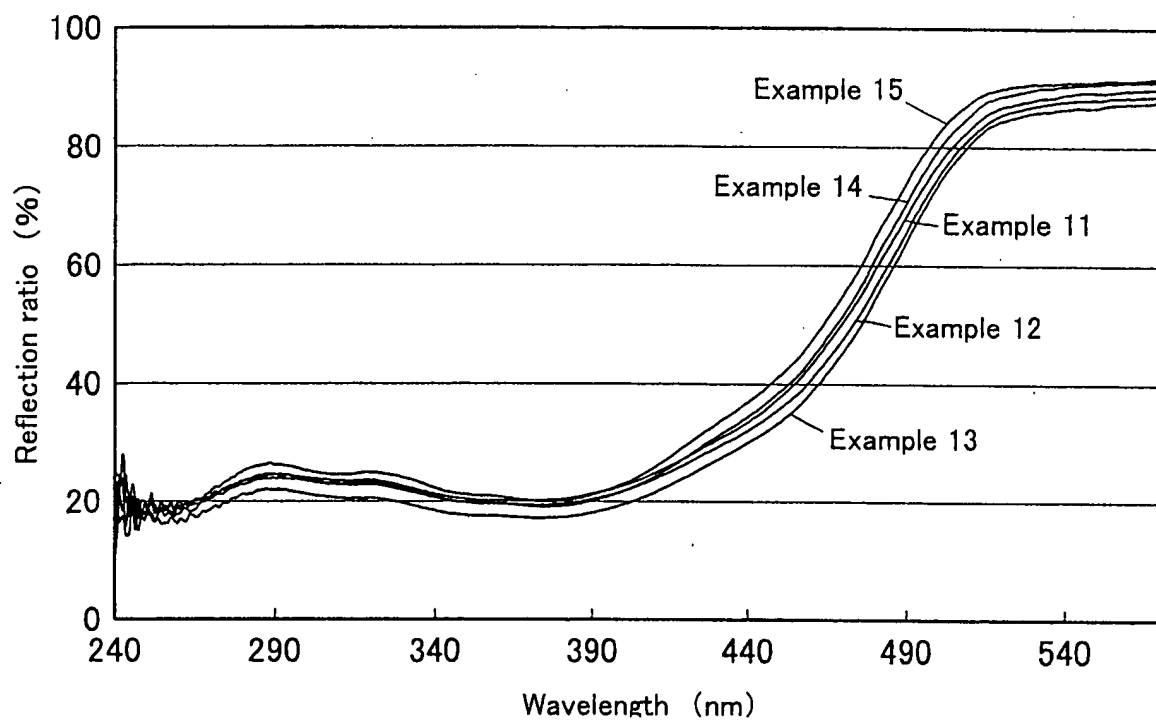


Fig. 12

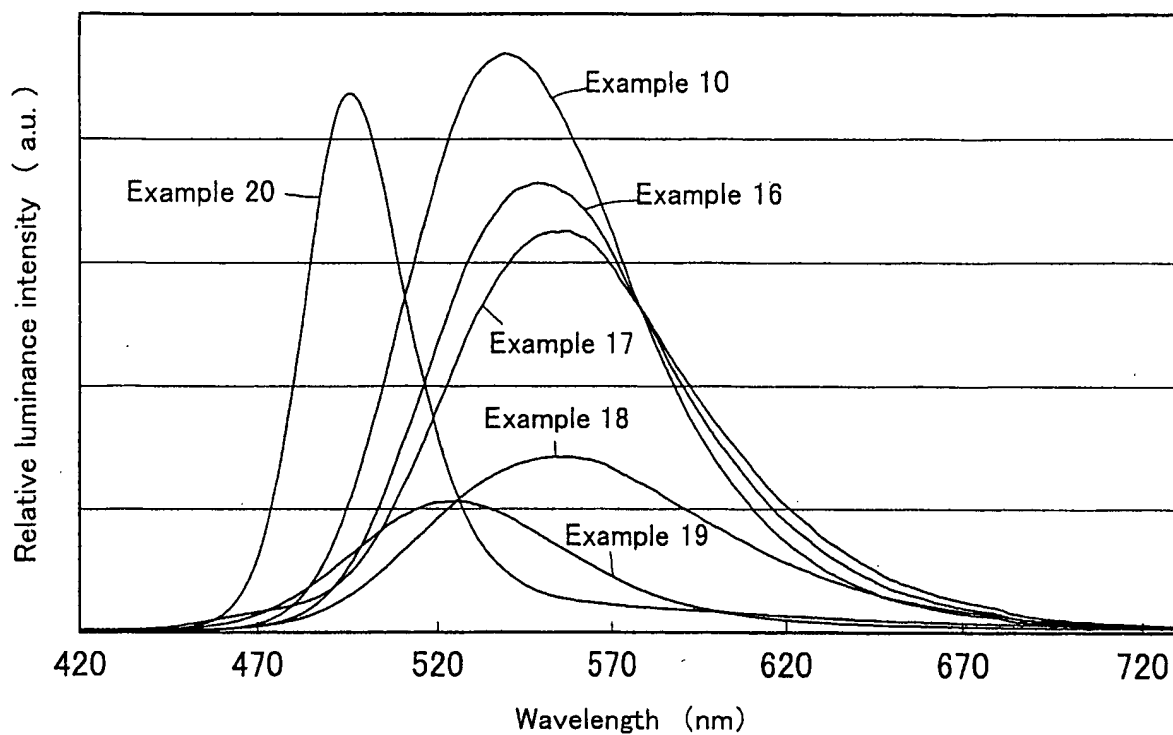


Fig. 13

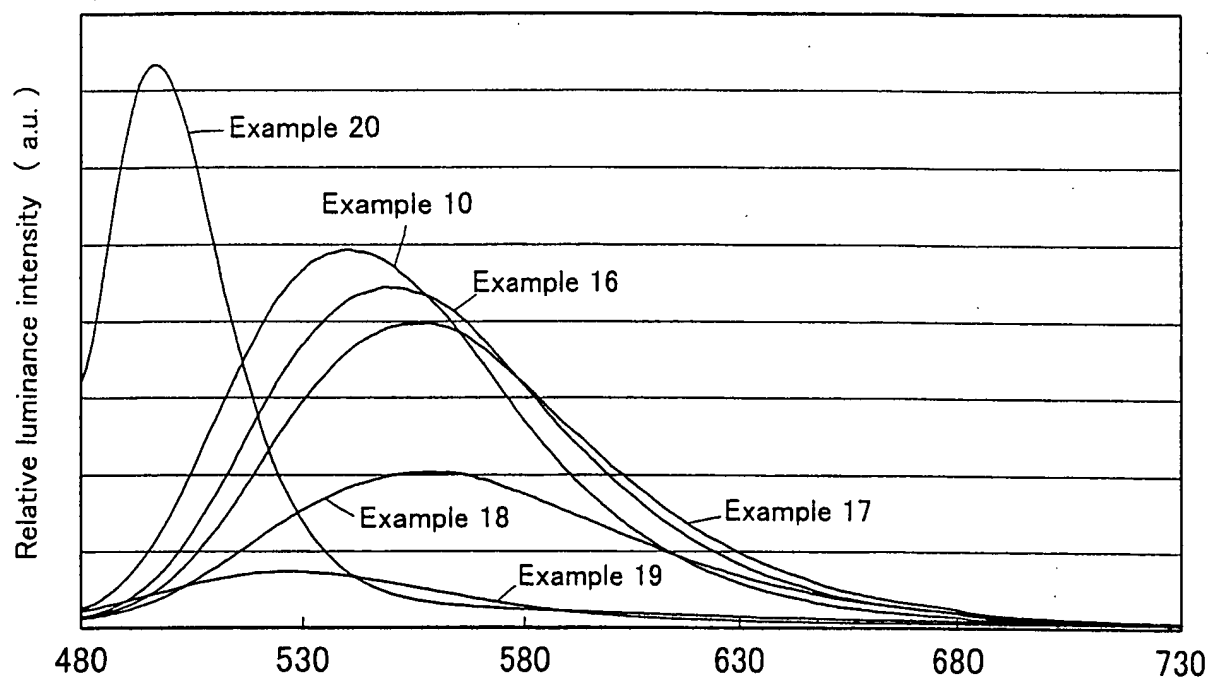


Fig. 14

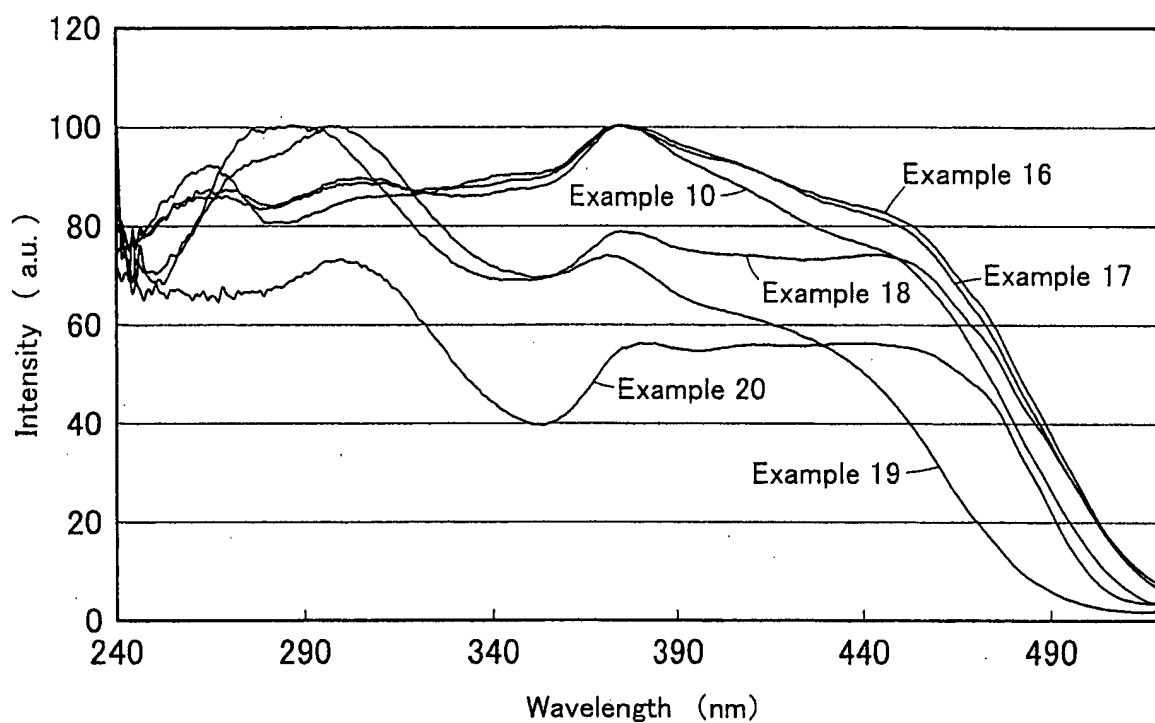


Fig. 15

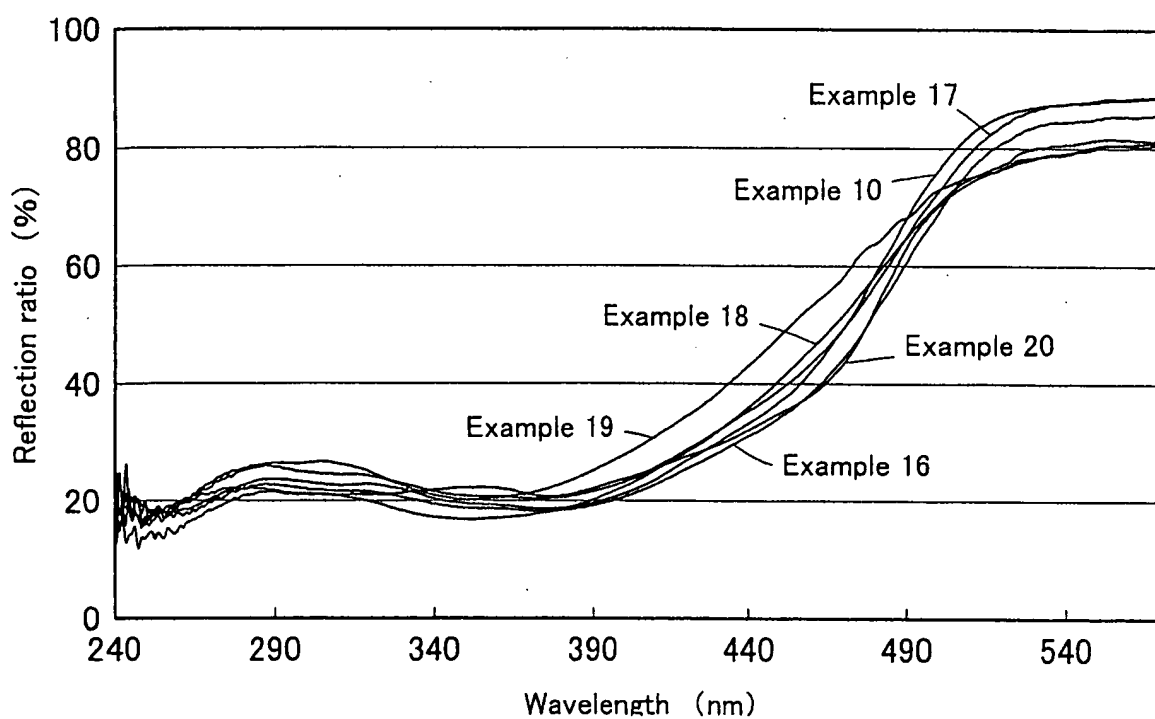


Fig. 16

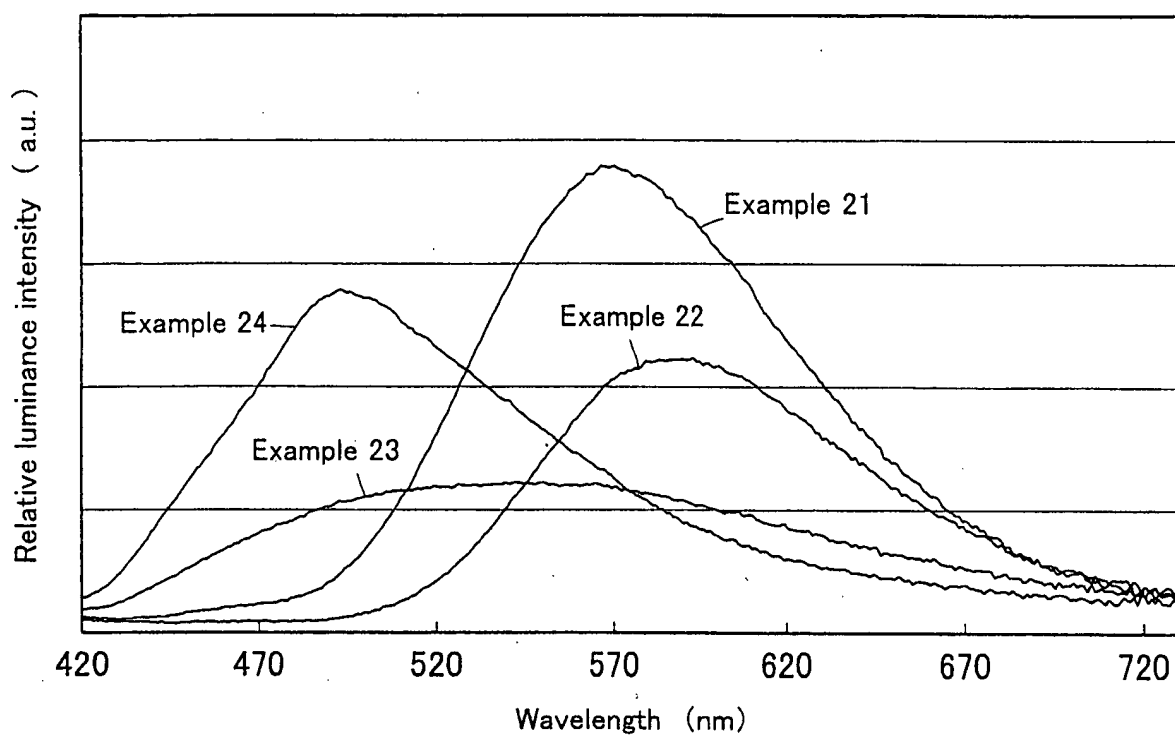


Fig. 17

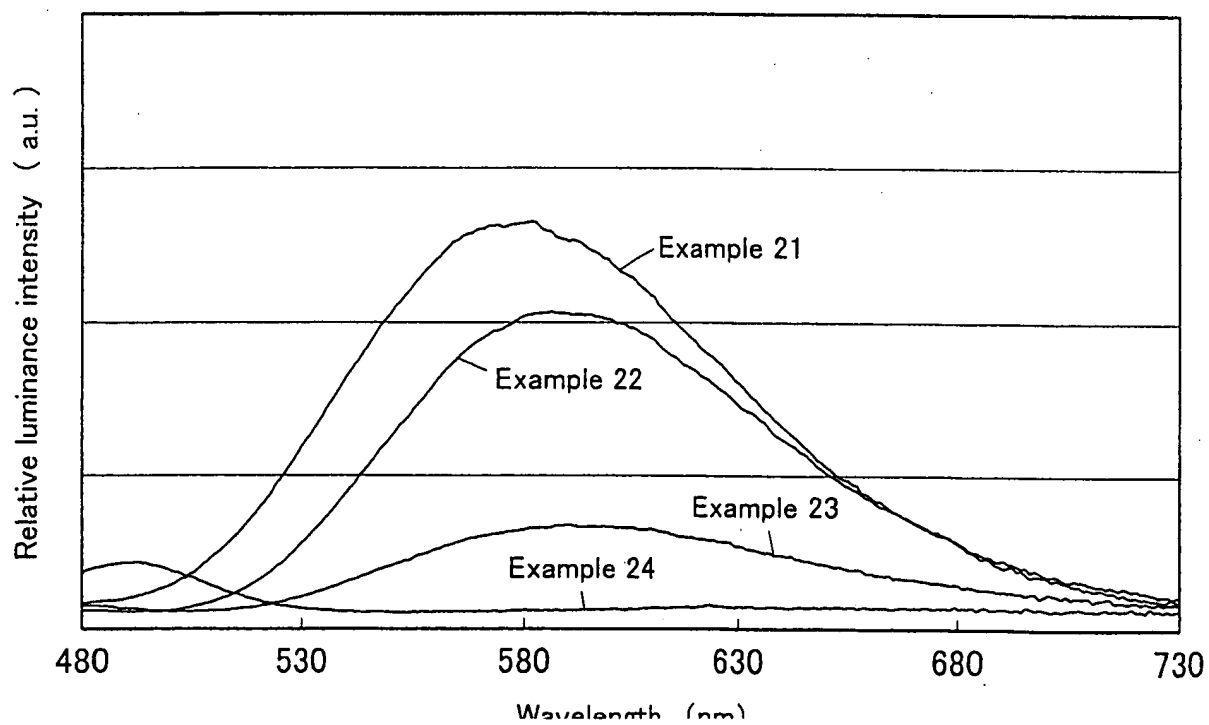


Fig. 18

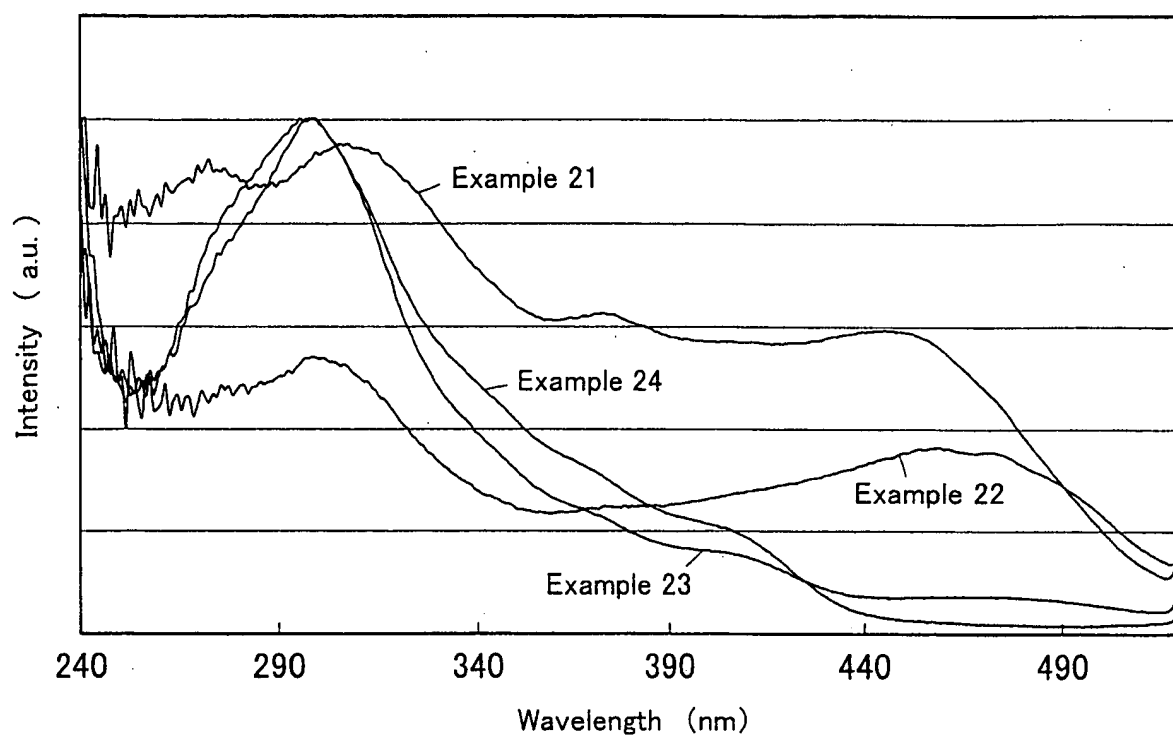


Fig. 19

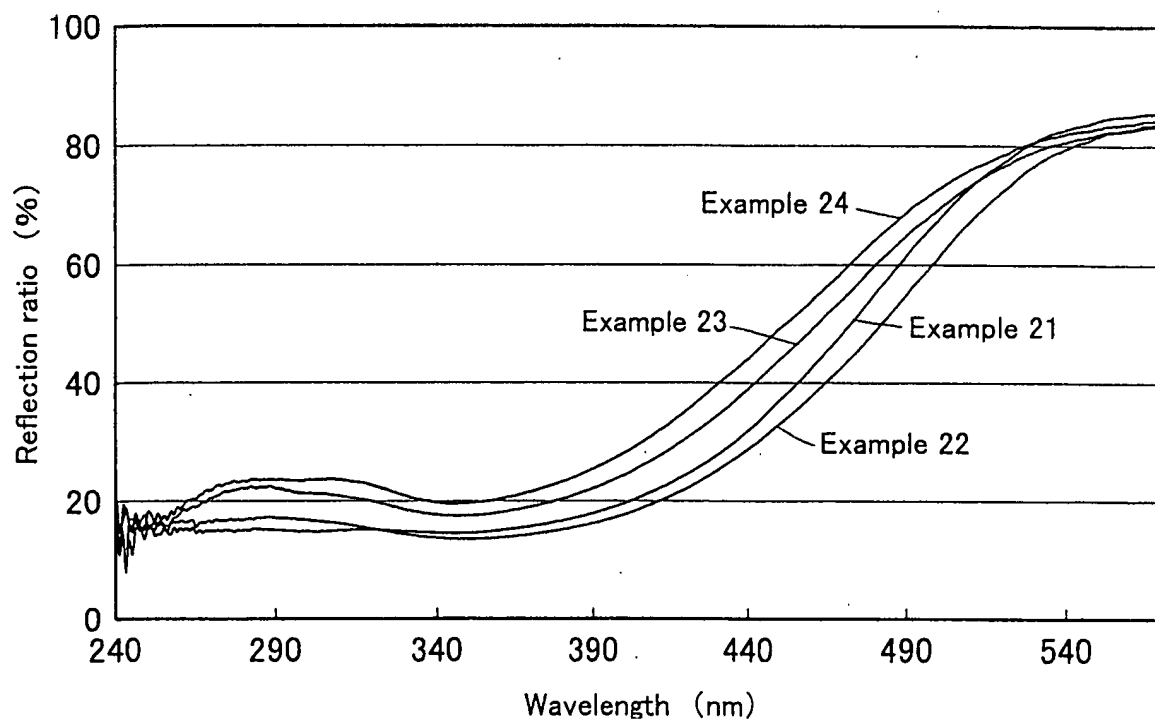


Fig. 20

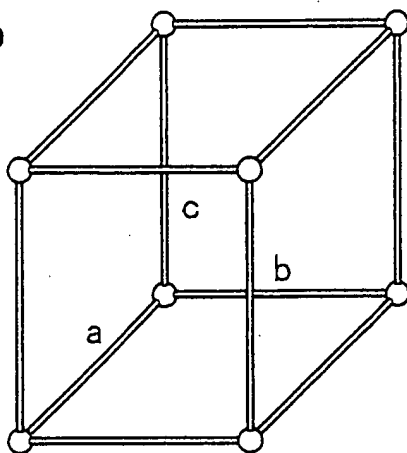


Fig. 21

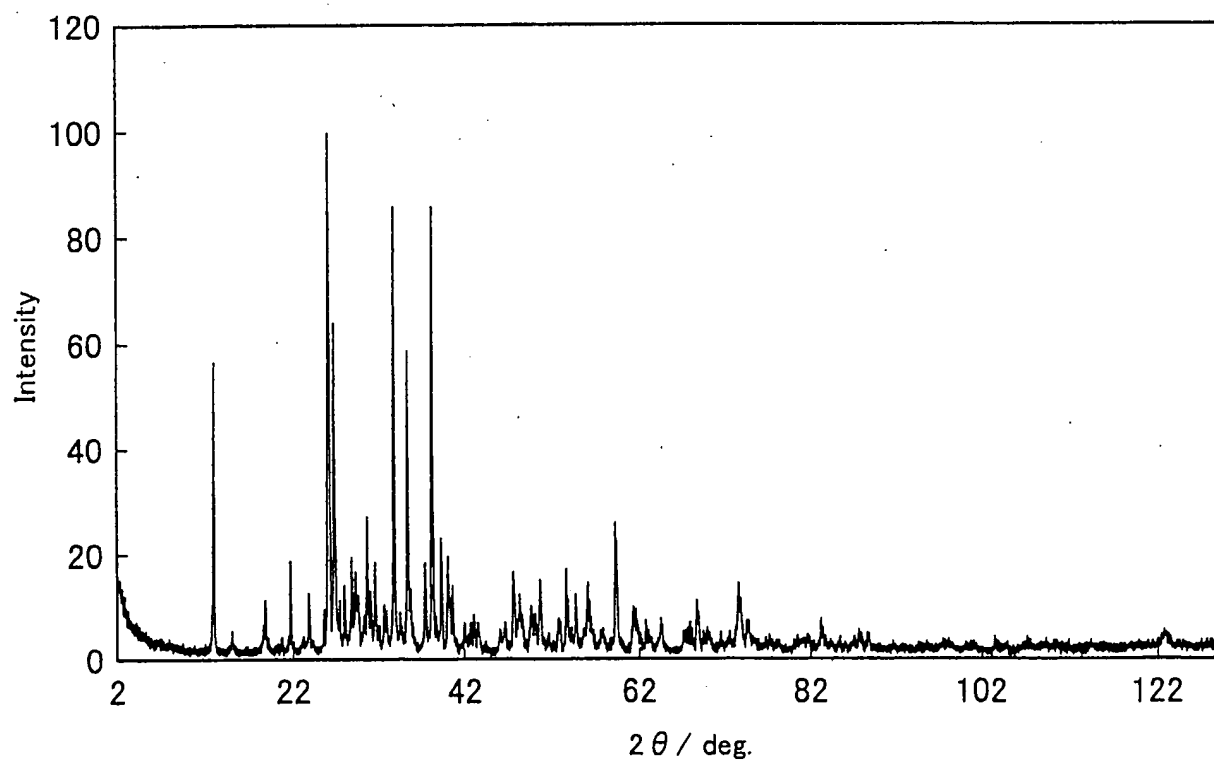




Fig. 22

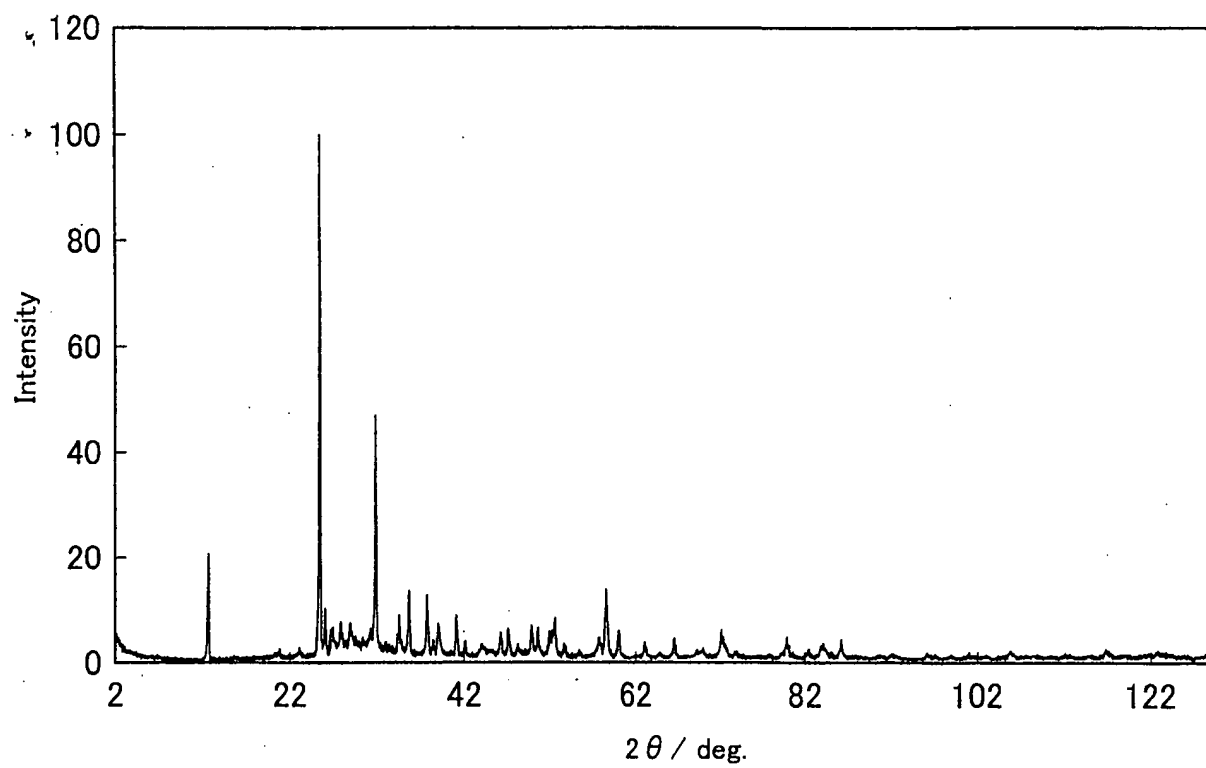
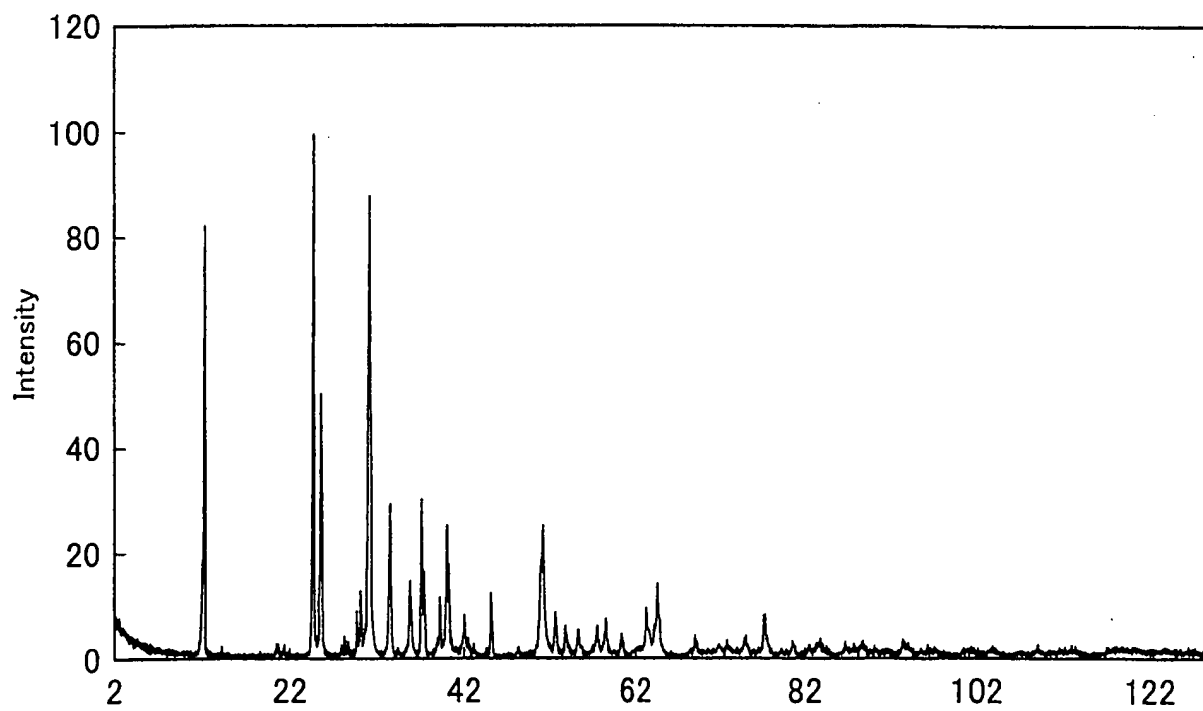


Fig. 23



## [DOCUMENT] ABSTRACT

## [Abstract]

[Problem to be solved] To provide an oxynitride fluorescent material capable of being excited by light having a wavelength range from near ultraviolet light to short-wavelength visible light and capable of emitting a luminescent color in a wavelength range from a green color to a yellowish color, and further having high luminescent intensity.

[Solution] This oxynitride fluorescent material is excited by light from an excitation light source in a wavelength range near 360-470 nm and emits luminescent light of a yellow-green color, wherein the oxynitride fluorescent material is expressed by formula  $LXMYOZN((2/3)X+(4/3)Y-(2/3)Z-\alpha):R$  (L is at least one kind of group II element selected from Be, Mg, Ca, Sr, Ba, and Zn; M is at least one kind of group IV element selected from C, Si, Ge, Sn, Ti, and Hf; O is oxygen; N is nitrogen; R is a rare earth element; and X, Y, Z, and  $\alpha$  each satisfies the following inequalities:  $0 < X < 1.5$ ,  $1.5 < Y < 2.5$ ,  $1.5 < Z < 2.5$ , and  $0 \leq \alpha < 1$ ).

[Selected Figure] Fig. 1

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